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REACTIVITY OF AROMATIC AND HETEROCYCLIC DERIVATIVES OF HYDRAZINE. IV. KINETICS OF BENZOYLATION REACTIONS OF HYDRAZINOACRIDINES IN CHLOROPHORM

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The kinetics of the benzoylation reaction of 8 hydrazinoacridines has been studied in chlorophorm in the temperature range of 25-55°C. Bimolecular reaction rate constants have also been found. The calculated parameters of the activation of the process indicate that the isokinetic relationship with the entalpic control holds within the reaction series. Kinetic data are in correlation according to the Arrhenius and Hammett equations. Regression analysis has been used in order to generate the two-parametric correlation equation with a cross term. Isoparametric values of correlating parameters (σ and T) have been calculated.

In order to continue the studies devoted to the establishing of the relationship between the structure reactivity and biological activity of the hydrazine derivatives, the kinetics of the benzoylation reaction of hydrazinoacridines (Table 1) has been examined in chlorophorm in the 25-55°C temperature range, described by the following equation:

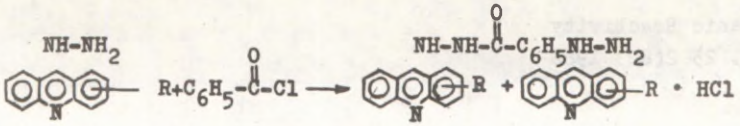

Table 1

Hydrazinoacridines

R	Melting t° °C	Pound % N	Brutto-formula	Calculated % N
H	171-172	19.81	$C_{13}H_{11}N_3$	20.08
2-Cl	258-260	16.97	$C_{13}H_{10}ClN_3$	17.24
3-Cl	172-173	17.46	$C_{13}H_{10}ClN_3$	17.24
4-Cl	231-232	17.52	$C_{13}H_{10}ClN_3$	17.24
2-CH_3	224-225	19.16	$C_{14}H_{13}N_3$	18.81
4-CH_3	129-130	18.99	$C_{14}H_{13}N_3$	18.81
2-OCH_3	143-144	17.33	$C_{14}H_{13}N_3O$	17.56
4-OCH_3	137-138	17.51	$C_{14}H_{13}N_3O$	17.56

The reaction rate constants were calculated according to changing of the benzoylchloride concentration in time, which was determined by argentometric potentiometric titration. The technique of kinetic measurements and processing of experimental data is similar to that used earlier. [1-3] The obtained results are given in Table 2.

Reaction rate constants depend on the substituents' nature and their position in the molecule of hydrazinoacridines.

It follows from Table 2 that the indroduction of electron-donor substituents (-CH_3, -OCH_3) leads to the growth of the reaction rate. The electron-acceptor substituents cause a contrary effect, analogous to the hydrazides of carbonic acids[1,2].

Table 2

Rate Constants of Benzoylation Reaction[a] of Hydrazinoacridines in Chlorophorm at Different Temperatures

R	k, $l \cdot mol^{-1} \cdot s^{-1}$ at T, K			
	298 K	308 K	318 K	326 K
H[b]	0.287 ±0.009	0.359 ±0.012	0.457±0.021	0.552±0.017
2-Cl	0.0404±0.0011	0.0582±0.0017	0.0837±0.0036	0.117±0.009
3-Cl[b]	0.0389±0.0016	0.0564±0.0024	0.0818±0.0026	0.112±0.006
4-Cl	0.0390±0.0021	0.0571±0.0034	0.0826±0.0017	0.113±0.009
$2-CH_3$	0.103 ±0.007	0.135 ±0.011	0.176 ±0.014	0.232±0.008
$4-CH_3$	0.0918±0.0010	0.125 ±0.012	0.174 ±0.012	0.229±0.010
$2-OCH_3$	0.125 ±0.012	0.164 ±0.008	0.218 ±0.015	0.277±0.028
$4-OCH_3$	0.400 ±0.023	0.478 ±0.018	0.590 ±0.017	0.671±0.032

a) The constants were calculated from 3 parallel experiments embracing 6-8 measurings.

b) The values of constants were taken from report[3].

The polyterme of logarithms of benzoylation reaction rate constants have a linear character. The latter is confirmed by great values of the Arrhenius equation correlation coefficients (Table 3).

This enabled us to find the activation energy E_A (kcal/mol) and the preexponential factor A according to the Arrhenius equation, the thermodynamic activation parameters (enthalpy $\Delta H^{\neq}$ (kcal/mol), entropy $\Delta S^{\neq}$ (e.u.), free energy $\Delta G^{\neq}$ (kcal/mol) according to Eyring (Table 4)).

The thermodynamic and kinetic activation parameters depend on the nature and position of the substituents in the molecule of hydrazinoacridines. The electron-donor substituents lead to the increase of the energy E_A, enthalpy $\Delta H^{\neq}$ and the free activation energy $\Delta G^{\neq}$, decreasing the absolute values of the activation entropy $\Delta S^{\neq}$. The electron-donor substituents bring about a contrary effect.

Table 3

The Arrhenius Equation Parameters of Benzoylation Reaction of Hydrazinoacridines,

$$\log k = \log k_0 + a_1 \cdot 10^3/T \qquad (1)$$

R	$-a_1$	$\log k_0$	r	S
H	0.9356±0.0099	2.597±0.060	0.9991	0.0036
2-Cl	1.5083±0.0058	3.665±0.042	0.9987	0.0023
3-Cl	1.5054±0.0046	3.642±0.028	0.9992	0.0033
4-Cl	1.5124±0.0034	3.667±0.034	0.9988	0.0034
2-CH_3	1.1461±0.0062	2.855±0.038	0.9994	0.0044
4-CH_3	1.3047±0.0043	3.338±0.026	0.9996	0.0040
2-OCH_3	1.1343±0.0084	2.902±0.031	0.9993	0.0031
4-OCH_3	0.7487±0.0072	2.115±0.052	0.9974	0.0063

Quantitative estimation of the substituent effect on the reactivity of hydrazinoacridines was carried out according to the Hammett equation (Table 5), using the σ-constant of quinoline[5]. The calculated reaction constants ρ of derivatives of hydrazinoacridines were rather small, though higher than the corresponding ρ values for 6-Cl-substituted 9-hydrazinoacridines, which were found in work[3]. It evidences about a decreasing reaction susceptibility in connection with the introduction of the electron-acceptor substituents. The ρ value is dropping if the temperature rises.

The mutually perturbational effect of both parameters (substituent constants σ and T) was estimated quantitatively according to the equation with one cross term[5]:

$$f(X_1X_2) = f_o + a_1X_1 + a_2X_2 + a_{12}X_1X_2 \qquad (3)$$

where f_o, a_1, a_2, a_{12} are the constants characterizing the susceptibility of the reaction series to the effect of the interacting parameters. The values of constants are given in Table 6.

Table 4

Kinetic (E_A and ln A) and Thermodynamic ($\Delta H^{\neq}$, $-\Delta S^{\neq}$, $\Delta G^{\neq}_{298}$) Activation Parameters of Benzoylation Reaction of Hydrazinoacridinee

R	E_A kcal/mol	ln A	r	S	$\Delta H^{\neq}$ kcal/mol	$-\Delta S^{\neq}$ e. u.	r	S	$\Delta G^{\neq}_{298}$ kcal/mol
H	4.27±0.16	5.96±0.19	0.9991	0.0085	3.90±0.08	48.0±2.7	0.9991	0.0092	18.2
2-Cl	6.91±0.21	8.45±0.11	0.9986	0.0052	6.29±0.10	43.8±1.4	0.9981	0.0087	19.3
3-Cl	6.86±0.31	8.34±0.51	0.9992	0.0050	6.27±0.15	43.9±1.8	0.9996	0.0112	19.4
4-Cl	6.93±0.16	8.45±0.16	0.9988	0.0081	6.31±0.11	43.8±1.5	0.9987	0.0087	19.4
2-CH_3	5.25±0.07	6.88±0.08	0.9994	0.0103	4.62±0.17	47.6±2.0	0.9993	0.0101	18.8
4-CH_3	5.98±0.06	7.70±0.08	0.9996	0.0096	5.35±0.16	45.3±1.9	0.9994	0.0010	18.8
2-OCH_3	5.20±0.11	6.69±0.10	0.9993	0.0073	4.58±0.19	47.3±1.7	0.9996	0.0076	18.7
4-OCH_3	3.43±0.10	4.88±0.12	0.9972	0.0148	2.81±0.23	50.9±2.8	0.9956	0.0166	18.0

Table 5.

Parameters of the Hammett Equation for Acylation of 9-Hydrazinoacridines at Different Temperatures

$$\log k = \log k_0 + a_2\sigma \qquad (2)$$

T,K	$a_2 = \rho$	$\log k_0$	r	S
298	-1.974±0.013	-1.109±0.019	0.9998	0.0059
308	-1.749±0.003	-0.974±0.004	0.9998	0.0009
318	-1.590±0.020	-0.835±0.028	0.9996	0.0087
328	-1.435±0.020	-0.715±0.029	0.9995	0.0086

Table 6.

Values of Susceptibility Parameters of Equation (3) and Isoparametric Value (IPV) of Correlation Parameters

Equation parameters	Variable/ cross term	Susceptibility factor	Numerical value	IPV
f_0	$\log K_0$	-	$(-6.712\pm0.008)\cdot10^{-3}$	
X_1	σ	a_1	1.112±0.005	β = 492 K
X_2	1/T	a_2	-283.4±11.3	X_1= -0.518
X_1X_2	$\sigma\cdot1/T$	a_{12}	-547.0±21.2	$X_2=2.03\cdot10^{-3}$

The IPV was calculated using the data of Table 6 according to the known formulae[5].

$$X_1 = -a_2/a_{12} \qquad X_2 = -a_1/a_{12} \qquad \beta = -a_{12}/a_1 \qquad (4)$$

It follows from the analysis of the data given in Table 6 that in the reaction series studied holds the isokinetic correlation with the value of the isokinetic temperature β=492 K. The value calculated according to formula (4) coincides with that calculated according to Eq.[5] (Table 7):

$$\log k_{T_2} = \text{const} + X \log k_{T_2} \qquad (5)$$

The existence of isokinetic correlation is proved by the linear correlation observed between $\Delta H^{\neq}$ -log k_T, $\Delta H^{\neq} - \Delta H^{\neq}$, E_A - log A, ρ - I/T (Table 8). The value of isokinetic tem-

perature β = 492 K exceeds the experimental temperature range, i.e. the enthalpic control of the reactivity is characteristic of the benzoylization reaction of hydrazinoacridines.

Table 7

Determination of Isokinetic Temperature β. Correlation Parameters of Eq. (5) of Benzoylation Reaction of Hydrazinoacridines

Temperature, K		X	r	S	β, K
T_1	T_2				
298	308	0.915	0.9998	0.0047	483
298	318	0.848	0.9990	0.0137	507
298	328	0.765	0.9990	0.0122	488
308	318	0.917	0.9995	0.0095	495
308	328	0.835	0.9994	0.0093	488
318	328	0.914	0.9947	0.0070	492

β = 492

Table 8.

Determination of Isokinetic Temperature. Correlation Parameters of Eqs. y = a + bX of Dependences of Kinetic and Activation Parameters of Benzoylation Reaction of Derivatives of Hydrazinoacridines and Isokinetic Temperature β.

X	y	a	b	r	S	β, K
$\log k_{298}$	$\Delta H^{\neq}$	$(1.45\pm0.16)\cdot10^3$	$(-3.46\pm0.19)\cdot10^3$	0.9974	0.201	492
$\log k_{308}$	$\Delta H^{\neq}$	$(1.62\pm0.08)\cdot10^3$	$(-3.77\pm0.17)\cdot10^3$	0.9985	0.216	492
$\log k_{318}$	$\Delta H^{\neq}$	$(1.90\pm0.38)\cdot10^3$	$(-4.07\pm0.18)\cdot10^3$	0.9980	0.065	495
$\log k_{328}$	$\Delta H^{\neq}$	$(2.07\pm0.37)\cdot10^3$	$(-4.48\pm0.17)\cdot10^3$	0.9979	0.255	493
$\Delta S^{\neq}$	$\Delta H^{\neq}$	$(27.1\pm1.5)\cdot10^3$	$(477\pm8$	0.9942	0.136	477
$\log A$	E_A	-1.33 ± 0.03	207 ± 2	0.9968	0.100	477
1/T	ρ	2.82 ± 0.13	-1399 ± 32	0.9980	0.033	496

The reliability of correlation parameters was checked by means of the Student[6] t - test, the probability level was found to exceed 95%.

Experimental

Reagents. The purification, drying and testing of the purity level of chlorophorm and benzoyl-chloride have been described earlier[1].

Hydrazinoacridines were synthesized according to the known methods[7,8]. Their purity was tested chromatographically, by means of the elemental analysis and determining the melting point (Table 1).

Kinetic studies were carried out according to methods[1]. The concentration of benzoyl chloride was determined by potentiometric titration with a 0.02 M solution of silver nitrate with silver and chlorosilver EVL-/m/ electrodes on an ionomer EV-74. The kinetics of benzoylation reaction was studied at 298, 308, 318, 328 K. Each experiment, including 6-8 measurements, was repeated three times. The accuracy of the obtained values was assessed using the method of mathematical statistics (the reliability level being 0.95)[9]. The thermodynamic activation parameters were calculated according to the known formulae[10] applying the least-squares method. The correlation analysis of the dependences found was performed on a computer using the program of the multiple regression analysis based on the algorithms of Draper and Smith.

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A STUDY OF ASSOCIATION OF ACETIC ACID AND PHENOL IN HYDROCARBON MEDIA.

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IR spectroscopy has been used in order to determine the dimerization constant of acetic acid and phenol in benzene and cyclohexane at 30°C taking into account the possible overlapping of the OH stretching frequencies of associates and monomers. It has been shown that in the systems studied (except for the acetic acid solutions in cyclohexane) no absorption of the associates was observed within the band of the OH stretching frequencies of the compounds' monomeric forms.

It is a well known fact that the overlapping of the absorption bands of the OH stretching frequencies characterizing the associated and monomeric forms of proton--donor compounds makes the interpretation of the IR spectra of their solutions in organic medium rather complicated. Therefore, a correct differentiation of these bands according to their intensity becomes the essential factor while estimating the self-association constant values of the compounds as well as the constants of complex formation with various nucleophiles.

The goal of the present paper is to determine the dimerization constants of acetic acid and phenol in benzene and cyclohexane taking into account the possible overlapping of the absorption bands of the OH stretching frequencies of

the associates and monomers connected with hydrogen bond.

The quantitative description of dimerization effect of the compounds examined on the optical density of their solvents (D), measured at the absorption peaks of the OH stretching frequencies was based on the assumption that the absorption registered is actually the superposition of the monomeric and dimeric absorption*.

Besides, the dependence of optical density of the solvents reduced to the unit of the thickness of the cell layer (l) on the analytical concentration (C) of acetic acid or phenol in solvents (Table 1) was given by system of equations (1):

$$\left.\begin{aligned} D/l &= x_1c_1 + x_2c_2 \\ C &= c_1 + 2c_2 \\ c_2 &= Kc_1^2 \end{aligned}\right\} \qquad (1)$$

where x_1, x_2 and c_1, c_2 denote respectively, the molar absorption coefficients and the concentration of monomeric and dimeric forms; K is the dimerization coefficient.

The dimerization constants were calculated at different values of x_1 and x_2 by means of taking the average of the solutions of system (2) of equation (1) using the data of all the experiments. Finding out the molar absorption coefficients

$$K = \frac{(x_2 - 2x_1)(D/l - x_1C)}{(2D/l - x_2C)^2} \qquad (2)$$

of the monomeric and dimeric forms of the compounds studied led to the calculation of the minimum coordinates of the $S = f(x_1, x_2)$, function, defined by (3),

$$S = \sum(K - \bar{K})^2 = f(x_1, x_2) \qquad (3)$$

---

* According to the literature data[1-3] the self-association of acetic acid and phenol in the studied concentration range (Table 1) leads, mainly, to the dimerization.

where $\bar{K}$ is the arithmetic mean of the dimerization constant.

The extremums of function S were found according to the coordinates x_1 and x_2 applying the method of scanning[4].

Table 1

Optical Densities (D) of Acetic Acid and Phenol (C) in Benzene and Cyclohexane at 30°C, Taken at the Peaks of ν_{OH} Bands of Monomers and Reduced to the Thickness Unit of Cell (l)

No	C, M	D/l, cm^{-1}	No	C, M	D/l, cm^{-1}
CH_3COOH in C_6H_6, ν_{OH}=3471 cm^{-1}			CH_3COOH in C_6H_{12}, ν_{OH}=3543 cm^{-1}		
1	0.0151	0.637	1	0.0130	0.147
2	0.0176	0.648	2	0.0259	0.233
3	0.0238	0.810	3	0.0389	0.295
4	0.0302	0.953	4	0.0518	0.354
5	0.0353	1.01	5	0.0648	0.404
6	0.0452	1.23	6	0.0778	0.464
7	0.0475	1.28	7	0.0907	0.513
8	0.0529	1.34	8	0.0997	0.534
9	0.0603	1.45	9	0.104	0.562
10	0.0705	1.62	10	0.112	0.588
11	0.0713	1.63	11	0.125	0.618
12	0.0754	1.65	12	0.137	0.654
13	0.0905	1.84	13	0.150	0.709
14	0.0950	1.90	14	0.162	0.745
15	0.106	2.04	15	0.174	0.766
16	0.120	2.19	16	0.187	0.823
PhOH in C_6H_6, ν_{OH}=3557 cm^{-1}			PhOH in C_6H_{12}, ν_{OH}=3617 cm^{-1}		
1	0.00751	1.46	1	0.00776	1.71
2	0.0150	2.84	2	0.0155	3.19
3	0.0225	4.22	3	0.0233	4.53
4	0.0300	5.45	4	0.0310	5.95
5	0.0376	6.79	5	0.0388	6.79
6	0.0451	8.05	6	0.0465	7.97
7	0.0526	9.28	7	0.0543	8.66
8	0.0601	10.3	8	0.0621	9.33

As an example, the obtained surface $S = f(x_1, x_2)$ for the C_6H_5OH-C_6H_6 system is given in Fig.1. Similar patterns were found also for systems CH_3COOH-C_6H_6, C_6H_5OH-C_6H_{12}. The

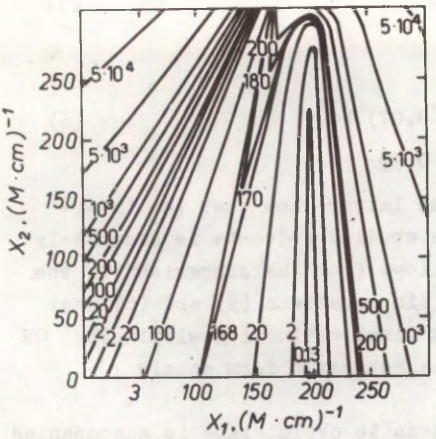

Fig. 1. The pattern of the $S=f(x_1, x_2)$ surface for the system $C_6H_5OH-C_6H_6$ at 30°C.

existense of clearly expressed minimums of function S if $x_2=0$ (the x_1 coordinate took various values) evidences about the absence of the associates' absorption in case of the OH stretching frequencies of the monomeric forms of acetic acid and phenol. The x_1, x_2 and $\bar{K}$ values calculated like this are given in in Table 2.

A low intensity of the bands of the OH stretching frequencies of monomers in the IR spectra of the acetic acid and cyclohexane solutions (Table 1) speaks about its practically complete dimerization. In such case, the insignificant contribution of the monomeric form into the system's total mass balance and a sharp increase of the relative noise level at the D values refer to the unreliable results (2). It was confirmed by the absence of the extremums of function S when calculating its pattern.

In order to calculate the dimerization constant of acetic acid in cyclohexane, we employed term (4), which is the solution of equation system (1) if $c_1 \ll c_2$.

$$K = \frac{2x_1^2C}{(2\ D/l - x_2C)^2} \qquad (4)$$

In case of the acetic acid and cyclohexane solutions, the data treatment according to a linear form (5) of this equation (Table 1) resulted in relationship (6).

$$\frac{D}{l\sqrt{C}} = \frac{x_1}{\sqrt{2K}} + \frac{x_2}{2}\sqrt{C} \qquad (5)$$

$$\frac{D}{l\sqrt{C}} = (1.17 \pm 0.02) + (1.75 \pm 0.07)\sqrt{C}, \qquad (6)$$

$$S = 0.03; \quad r = 0.99$$

Statistical parameters of the latter show that the intermolecular interaction in the studied solvents is adequately described by Eq. (4). It follows from the comparison of the coefficients in case of $\sqrt{C}$ in equations (5) and (6) that the value of the acetic acid dimer extinction within the OH stretching frequencies of the monomeric form equals 3.5 ± 0.1 $M^{-1} \cdot cm^{-1}$.

The transition from benzene to cyclohexane is accompanied by approximately equal frequency shifts of the ν_{OH} bands of the acetic acid and phenol monomers (Table 1), therefore we supposed that the solvent effect on the extinction of the acetic acid and phenol monomers (Table 2) is expressed by a proportinnal variation of these values. It enabled us to quantitatively estimate the coefficient of molar absorption ν_{OH} of the acetic acid monomers and its dimerization constant in cyclohexane (comparing the free terms of (5) and (6):

$$x_1 = 80.8\ M^{-1} \cdot cm^{-1}; \quad K = 2370 \pm 60\ M^{-1}.$$

Thus, the results of the present work show the absence of overlapping of the ν_{OH} bands of the monomeric and dimeric forms within the OH stretching frequencies of the acetic acid and phenol in the IR spectra of the CH_3COOH-C_6H_6, C_6H_5OH-C_6H_6 and C_6H_5OH-C_6H_{12} systems.

This permitted to calculate correctly the values of dimerization constants of acetic acid and phenol in the given systems according to the intensity peaks of the ν_{OH} band

Table 2

Molar Absorption Coefficients of Monomers (x_1) and Dimers (x_2) at Peaks of ν_{OH} Bands of Monomers and Dimerization Constants (K) of Acetic Acid and Phenol in Benzene and Cyclohexane at 30°C.

x_1, $M^{-1} \cdot cm^{-1}$	x_2, $M^{-1} \cdot cm^{-1}$	K, M^{-1}	Reference data[5] K, M^{-1} (°C)	Method of measuring
			CH_3COOH in C_6H_6	
66.1	0	38.8±0.7	129 (30.6)	Phase distribution
			27.5 (20.0)	IR spectroscopy
			CH_3COOH in C_6H_{12}	
80.8*	3.5	2370±60	20900 (25.0)	Dielectric measurements
			7500 (29.4)[2]	NMR spectroscopy
			PhOH in C_6H_6	
198	0	1.4 ±0.1	0.617 (30.0)[3]	IR spectroscopy
			0.575 (25.0)	Measuring of vapor pressure
			0.129 (25.0)	Calorimetry
			PhOH in C_6H_{12}	
242	0	6.6 ±0.3	0.1 (25.0)	Calorimetry

* Value, calculated from the x_1 of acetic acid and phenol in benzene and phenol in cyclohexane.

maximums of the monomeric forms . The dimerization constant values of acetic acid can be determined in cyclohexane, via the intensity of the bands of the monomers of OH stret - ching frequencies only on condition that the contribution of the dimeric component is taken into consideration.

Experimental

Acetic acid, phenol and solvents were purified according to the ordinary methods.

The IR spectra of the systems were measured on a spectrophotometer Specord-IR-75, the frequency range being 3100--3700 cm^{-1}. The length of the cell layers did not exceed 0.1 cm. Scanning rate was 10 $cm^{-1} \cdot min^{-1}$. Each spectrum was registered twice at least.

The solutions having necessary concentration were prepared using the gravimetric method and that of gradual dilutions.

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A STUDY OF COMPLEX FORMATION OF ACETIC ACID AND PHENOL WITH AMINES IN HYDROCARBONS

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IR spectroscopy was applied to study the complex formation of acetic acid and phenol with aniline, pyridine, N-methylpiperidine and piperidine in benzene and cyclohexane at 30°C. Equilibrium constants of formation of proton-donor--amine complexes, their composition being 1:1 and 2:1, are obtained. LFER of the formation of equilibrium of 1:1 complexes in benzene and cyclohexane at 30°C has also been dealt with.

It should be mentioned that the quantitative information on the proton donors complex formation with various nucleophiles in hydrocarbons is rather limited at the moment, therefore it is not easy to sufficiently describe the kinetics of nucleophilic substitution reactions proceeding in the above mentioned solvents when the proton donor molecules act as catalysts.

The present work is aimed at the quantitative analysis of the reactions of formation acetic acid and phenol complexes with amines of various structure in benzene and cyclohexane at 30°C.

According to our assumptions, the complex formation in these solvents can be described by the system of combined

equilibria (1):

$$2A \overset{K_1}{\rightleftharpoons} A_2$$

$$A + B \overset{K_2}{\rightleftharpoons} AB$$

$$A + AB \overset{K_3}{\rightleftharpoons} A_2B$$

where A and B denote the proton-donor and amine molecules, respectively. K_1 is the proton-donor[1] dimerization constant: K_2 and K_3 are the equilibrium constants of the proton-donor-amine complexes whose composition is correspondingly 1:1 and 2:1[2,3]. K_2 and K_3 have been calculated as the coefficients of Eq.(2) which has been found via the simultaneous solving of the mass balance equations for equilibria (1):

$$C_1(\alpha - 1) = 1/K_2 - K_3C_1^2(2\alpha - 1), \qquad (2)$$

where α denotes the function of the monomeric form concentration of proton-donor (C_1), its analytical concentration (C) and the amine analytical concentration (B).

$$\alpha = \frac{B}{C - 2K_1C_1^2 - C_1} \qquad (3)$$

The C_1 values were established by means of the IR spectroscopy from the intensity peaks of the absorption band maximums of the OH stretching frequencies of monomeric molecules acetic acid and phenol and their molar absorption coefficients[1].

Tables 1 and 2 present the values of equilibrium constants of complex formation for different systems studied in the present work. The results obtained indicate that the intermolecular interactions of these donors and acceptor protons in the solvents studied can really be described with the system of equations (1). Thus, the values of correlation coefficients of equation (2) equal 0.98-0.99 in case the systems' equilibrium is achieved by formation of the 2:1 H

complexes.

Table 1.

Values of Equilibrium Constants of Formation of 1:1 (K_2) and 2:1 (K_3) H-Complexes in Systems Formed by Acetic Acid and Phenol with Various Amines in Benzene at 30°C

No	Proton donor C, M	Proton acceptor B, M	K_2 M^{-1}	K_3 M^{-1}
1	CH_3COOH 0.0805	$C_6H_5NH_2$ 0.0307-0.123	16±1	0
2	CH_3COOH 0.0805	C_5H_5N 0.0229-0.0916	40±5	0
3	CH_3COOH 0.0705	$C_5H_{10}NCH_3$ 0.0104-0.0415	170±40	39±6
4	CH_3COOH 0.0705	$C_5H_{10}NH$ 0.00871-0.0348	500±100	34±3
5	C_6H_5OH 0.0637	$C_6H_5NH_2$ 0.0311-0.126	1.30±0.04	0
6	C_6H_5OH 0.0601	C_5H_5N 0.0229-0.0916	24.0±0.5	0
7	C_6H_5OH 0.0637	$C_5H_{10}NCH_3$ 0.0206-0.0823	59±2	0
8	C_6H_5OH 0.0637	$C_5H_{10}NH$ 0.0205-0.0819	84±2	5.5±0.2

It can be seen from the tables that variation of formation constants of the complexes having a varied composition is in agreement with the changes of the amines' basicity.

The pK_{BH^+} values of aniline, pyridine, N-methylpiperidine and piperidine in water are 4.58, 5.23, 10.08 and 11.12[4]. In all cases, the transition from cyclohexane to benzene is followed by a drop of the K_2 and K_3 values. It can most probably be explained by strengthening of some specific solvation types of the molecules of initial products with the solvent molecules competing with complex formation, i.e. by the nucleophilic solvation of hydroxylic hydrogen atoms of proton donors and by

the electrophilic solvation of nitrogen atoms of amines.

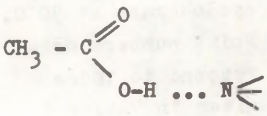
Table 2

Values of Equilibrium Constants of Formation of 1:1(K_2) and 2:1(K_3) H-Complexes in Systems Formed by Acetic Acid and Phenol with Various Amines in Cyclohexane at 30°C

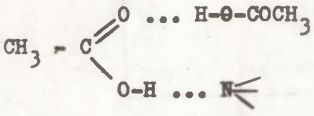
No	Proton donor C, M	Proton acceptor B, M	K_2 M^{-1}	K_3 M^{-1}
1	CH_3COOH 0.0817	$C_6H_5NH_2$ 0.0300-0.120	18±3	0
2	CH_3COOH 0.0817	C_5H_5N 0.0202-0.0806	180±10	0
3	CH_3COOH 0.0759	$C_5H_{10}NCH_3$ 0.00989-0.0396	1400±500	1800±300
4	CH_3COOH 0.0759	$C_5H_{10}NH$ 0.0280-0.0403	9000±3000	18600±800
5	C_6H_5OH 0.0621	$C_6H_5NH_2$ 0.0300-0.120	5.9±0.3	19±2
6	C_6H_5OH 0.0621	C_5H_5N 0.0199-0.0796	37±5	58±8
7	C_6H_5OH 0.0610	$C_5H_{10}NCH_3$ 0.0198-0.0791	83±3	48±1
8	C_6H_5OH 0.0610	$C_5H_{10}NH$ 0.0201-0.0805	101±2	77±1

The analysis of the K_2 values (Tables 1 and 2) prove that in the systems studied, acetic acid forms with amines remarkably more stable 1:1 complexes than phenol. This statement does not concern the formation of the 2:1 complexes with aniline and piperidine in cyclohexane, i.e. if in case of the systems with phenol are formed the 2:1 hydrogen bond complexes, acetic acid does not form them. This is in keeping with the conclusion of paper[3], where it is shown that the possibility of formation of the 2:1 complexes is decreasing with the increase of proton donor properties of the acids. Dependence of the K_3 values on the acids' proton-donor activity in their

reactions with aliphatic amines (Tables 1 and 2, Nos 3,4 and 7,8) has the opposite character. Relatively high values of equilibrium constants of complex formation seem to be conditioned by a high level of proton transfer from an acid to the base in a molecular complex (I)[2,3]. As a result, the nucleophility of the hydrogen atom of the proton-donor carbonylic group is growing, thus favoring the increase of the free energy of another hydrogen bond formation in complex (II).



I



II

The comparison of the K_2 values in case of similar complexes in various solvents (Tables 1 and 2) yields straight lines with high correlation coefficient values (Fig.1), which most probably evidences about the following statements:

1. In case of a fixed proton donor, in the solvents examined, the 1:1 complexes keep a similar structure type with various amines.

2. The interaction of acetic acid with amines in characterised by a remarkably higher level of proton transfer in a molecular complex and consequently, also by a more substantial charge redistribution in it. The aforesaid as well as the differences in the solvation energies of the acetic acid and phenol molecules in the basic state are reflected in the specific dependencies (with reference to the proton-donor structure), which express the linear free energy relationship of complex formation in various solvents.

It should be said in conclusion that the dimerization constant[1] and those of formation of the phenol complexes with the 1:1 amines make up a united correlation dependence (Fig. 1, point A) in the studied solvents, while the acetic acid dimerization constant[1] considerably deviates from the dependency describing the complex formation of this proton donor with amines (Fig. 1, point B).

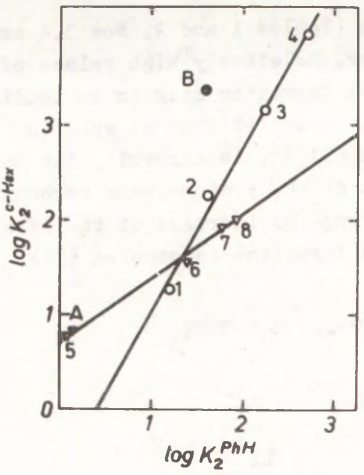


Fig.1. Interdependence of the logarithms of dimerization constants (●, ▼), of formation of the 1:1 acetic acid (○, ●) and phenol (▽, ▼) complexes with various amines in benzene and cyclohexane at 30°C. Point numbers correspond to those given in Tables 1 and 2.

This must be caused by the identical structure of the dimers of phenol and its H-complexes with amines but the dimers of acetic acid (of cyclic form) and its hydrogen-bond associates with amines seem to have different structure.

Experimental

The amines, acetic acid, phenol and solvents used were purified according to traditional methods.

The IR spectra of the systems studied were registered on a spectrophotometer Specord-IR-75, the frequency range being 3100-3700 cm^{-1}. Each spectrum was registered three times at least. The length of a cell layer was 0.1 cm. In some occasions, the concentration of amines was measured four times. The proton donor concentration in solvents remained constant. The values of analytical cofficients of reagents are given in Tables 1 and 2.

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INTERACTION OF n-ALKYLCHOLINEBENZILATES WITH CHOLINESTERASES

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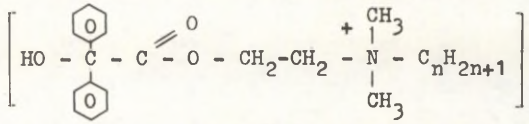
Several esters of benzilic acid are known as the pharmacologically active compounds which are used as the ligands in a biochemical assay of muscarinic cholinoreceptor[1,2]. However, it is necessary to take into account the possibility of binding these compounds by the other components in the receptor preparation, especially by cholinesterases since the active centers of these enzymes are complementary to the structure of acetylcholine and can be characterized with the same specificity factors[3] as the receptor.

In this paper we have studied the reversible inhibition of acetylcholinesterase and butyrylcholinesterase hydrolysis of acetylcholine by a series of benzilic esters with the structure



(1)

with the aim of determining their efficacy of interaction with the enzymes.

Experimental

The alkyl derivatives of cholinebenzilates with the structure (1)(n = 1 - 9), are synthesized as described earlier[1]. Acetylcholinesterase (AChE) - preparation from cobra venom, purified by affinity chromatography, received from the Institute of Chemical and Biological Physics, AS ESSR, the specific activity was 11,5 μkat/mg. Butyrylcholinesterase (BChE) - preparation from horse serum, purified by gelchromatography, was purchased from the Mechnikov Institute of Sera and Vaccine, Moscow, the specific activity was 20 nkat/mg. The enzyme activity was measured titrimetrically following acetylcoline iodide hydrolysis residual velocities[4] making use of the pH-stat (Radiometer Titrigraph, Denmark, set of PHM 82, TTT 80, ABU 80, REC 80 Servograph). The experiment was carried out at pH 7.5, 25°C in 0.15 M KCl.

The dissociation constants of the complex of benzilates with the enzyme were measured in pseudomonomolecular conditions $[S]_o \ll K_{M(app.)}$ of the substrate reaction at different concentrations of the reversible inhibitors. Reaction mixture contained 10^{-3}-10^{-6} M of ligand and 10^{-8} of enzyme.Acetylcholine iodide was added to this mixture to get the final concentration of 10^{-5} M and then the kinetic curve was followed during 3-5 periods of half-life (2-14 min). From these kinetic curves the values of the apparent pseudofirst-order rate constants were calculated[5] :

$$[P] = [S]_o \cdot (1-e^{-k_{app.} \cdot t}), \qquad (2)$$

where [P] is the concentration of the acetic acid, $[S]_o$ denotes the substrate concentration, $k_{app.}$ - apparent rate constant, t - time,

The values of the constants $k_{app.}$ were calculated from the kinetic curves making use of the linear least squares method[6].

In the presence of the reversible inhibitor of the enzyme we obtain[5]:

$$k^{i}_{app.} = k^{o}_{app.} \cdot \frac{[I]}{K_D + [I]} \quad (3)$$

The values of the constants K_D were calculated making use of the linear transformation of Eq. (3) in the coordinates $1/k^{i}_{app.}$ and $[I]$:

$$\frac{1}{k^{i}_{app.}} = \frac{1}{k^{o}_{app.}} + \frac{1}{k^{o}_{app.}} \cdot \frac{1}{K_D} \cdot [I] \quad (4)$$

The calculations were carried out on a PC "Commodore Plus/4" (England).

Results and Discussion

In Table 1 are given the K_D values for the reversible inhibition of AChE and BChE by n-alkyl derivatives of cholinebenzilates.(1).It is evident that the regular **alteration** of the structure of benzilic esters brings about an increase in the binding efficiency of these compounds with the both enzymes, in the other words, the tendency of **decreasing** K_D with the growing of n is observed.

Table 1.

Inhibition of Cholinesterases with n-Alkylsubstituted Cholinebenzilates (1).

n	$K_D \cdot 10^4$, M AChE	$K_D \cdot 10^6$, M BChE	π_{eff}
1	16.6 ± 1.1	18.2 ± 1.5	4.3
2	11.9 ± 2.0	13.5 ± 0.4	4.8
3	7.88± 0.13	8.10± 0.62	5.3
4	7.12± 0.12	2.61± 0.09	5.8
5	4.65± 0.22	1.25± 0.02	6.3
6	2.90± 0.04	1.10± 0.01	-
7	1.78± 0.01	1.05± 0.01	-
8	1.23± 0.02	0.904±0.016	-
9	1.02± 0.04	0.768±0.002	-

It is seen from structure (1) that the only varying element in the studied series of the compounds is the n-alkyl chain connected with the quaternary nitrogen. As far as the lengthening of this carbohydrate substituent changes the volume of the molecule and its hydrophobicity, it is natural to suppose that the latter factor determines the binding efficiency of the benzilates with the active centers of the enzymes. On the other hand, it is seen from Table 1 that the K_D values for BChE are about 100 times smaller if compared to the K_D values for AChE. Therefore, the binding centers of these enzymes are different thus bringing about the different binding efficiencies of the ligands.

Formula (1) of the studied ligands shows that the derivatives of cholinebenzilates may be considered the series of alkylammonia with the structure

$$R - \overset{\overset{CH_3}{|}}{\overset{+}{N}} - \overset{\overset{CH_3}{|}}{} - C_nH_{2n+1} \cdot \qquad (5)$$

For the ammonium compounds with $R=CH_3$ there are the data in literature concerning their inhibition characteristics with AChE and BChE [7,8]. Besides, it is necessary to correct the data from [7], taking into account the effect of the excess of the substrate concentration on the inhibitory properties, and to transfer the I_{50} to the values of K_D. It was done making use of the values of $K_D = 2{,}50 \cdot 10^{-3}$ M [9] for the BChE inhibition by tetramethylammonia and $K_D = 2{,}33 \cdot 10^{-3}$ M for AChE [8].

Hence, the values from literature of pK_D for the ammonium ions are compared with the pK_D values for benzilic esters in Figures 1A and 1B as the dependences of these constants on n. For AChE these dependences practically coincide. Consequently, the same structural element of the ligand is used for binding of the both ligand types in the active center of the enzyme. It means that the residue of the benzilic acid does not take part in the interaction of the ligand and

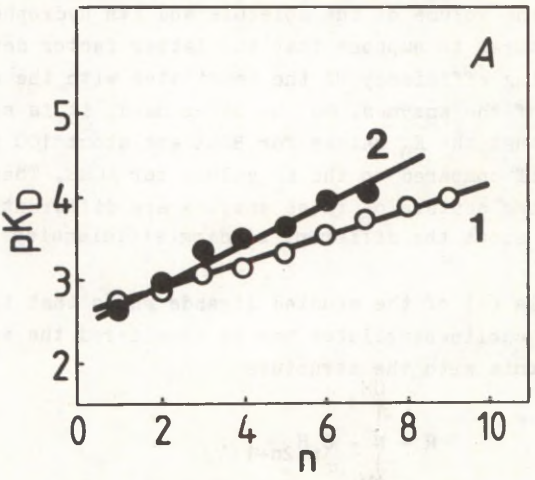


Fig. 1A. Plot of pK_D vs. n for acetylcholinesterase interaction with n-alkylsubstituted cholinbenzilates (1) and n-alkyltrimethylammonium ions (2, data from[7]).

the enzyme, despite the significant contribution of this group into the general hydrophobicity of the molecule. These results point to the discrepancy between the size of the hydrophobic binding center and **the ligand molecule in this area** of the binding site where the ester group of the benzilate is located. This conclusion agrees well with the earlier ideas about the structure of the active site of AChE[10].

In the case of BChE, the initial parts of the dependences of pK_D **on** n for alkylammonium ions and alkylbenzilates have the same slope, however the intercepts of the ordinate differ significantly. Accordingly, in this dependence

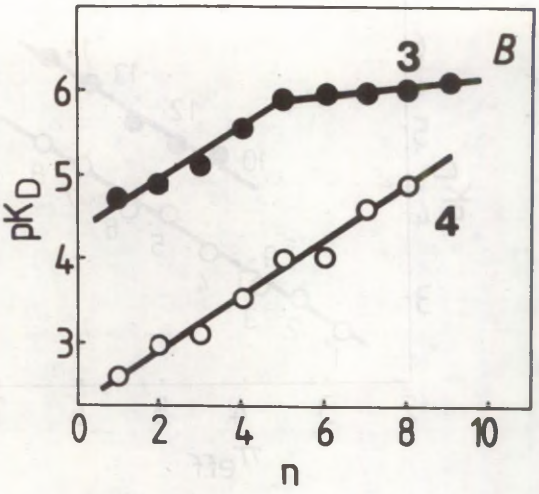


Fig 1B. Plot of pK_D vs. n for butyrylcholinesterase interaction with n-alkylsubstituted cholinbenzilates (3) and n-alkyltrimethylammonium ions (4, data from [7]).

the break is revealed at the change of n from 5 to 6, which is absent in the case of n-alkylammonium ions. Consequently, the dispositions of n-alkyl substituents of these compounds in the active center of BChE do not coincide with each other. Moreover, it can be concluded that the hydrophobicity of the acyl part of benzilates is involved in their binding to BChE. For a more detailed examination of the problem, a plot of pK_D vs. $\pi_{eff.}$, is depicted in Fig. 2. which characterizes the whole hydrophobicity of the ligand molecule in case of a series of ammonium ions. The latter values have been calculated proceeding from the additive scheme of calculation

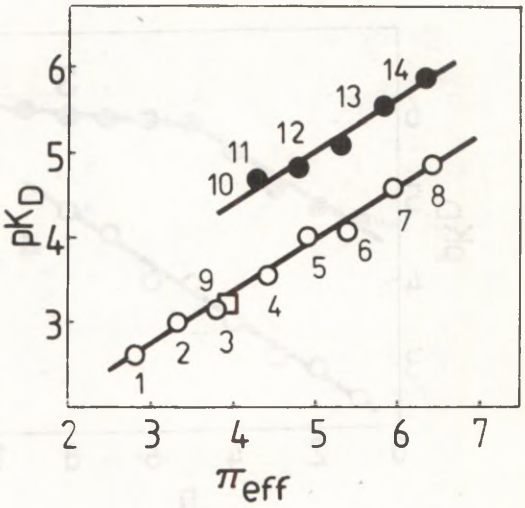


Fig. 2. Plot of pK_D vs. π_{eff} for butyrylcholinesterase inhibition with n-alkyl(trimethylammonium ions (1-8)[7] and trimethylphenylammonium ions (9)[12] and n-alkylsubstituted cholinebenzilates.(10-14).

of the hydrophobicity constants of complex molecules as reported in[11]. The calculation of π_{eff} was carried out without taking into account the contribution of ammonium ion as this structural fragment is met in all compounds discussed. Moreover, a fully correct account of this increment is connected with certain difficulties.

In Fig. 2 is depicted the plot of pK_D vs. π_{eff} for BChE inhibition with n-alkyltrimethylammonium ions $(CH_3)_3 - \overset{+}{N} - C_nH_{2n+1} \cdot X^-$, (n= 1-8) (the results from[7]), trimethylphenylammonium[12] (pK_D = 3.2 and π_{eff} = 3.9) and with benzilates (1) at n=1-5. For all simple ammonium ions

an overall linear dependence can be observed:

$$pK_D = pK_D^o + \varphi \cdot \pi_{eff} \quad , \qquad (6)$$

where $pK_D^o = 0.9 \pm 0.2$ and $\varphi = 0.6 \pm 0.1$. The data for benzilates deviate from these dependences, although in case of these compounds equation (6) is valid, according to which $pK_D^o = 2.0 \pm 0.3$ and $\varphi = 0.6 \pm 0.1$.

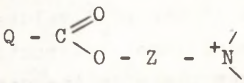
It is typical that the φ values for the both series coincide. The difference in the pK_D^o values gives evidence about the fact that an additional interaction with the active center of the enzyme takes place in the case of binding of benzilates, or the hydrophilic groups of the benzilates do not take part in this process. That increases the binding efficacy of the ester by one pK_D unit.

However, the present data do not allow to discriminate between these possibilities, we can summarize that the large difference in the pK_D values for AChE and BChE is connected with unequal volume of the appropriate hydrophobic areas on the active surface of cholinesterases. This conclusion is in accordance with the well-known concept of a larger volume of the active center of BChE in comparison with AChE. At the same time, it must be emphasized that in the case of AChE there are no steric hindranoes in the binding process as the pK_D values for the appropriate benzilates and ammonium salts are practically the same. This means that the active center of AChE lacks the hydrophobic region in the binding area of the acyl fragment of the substrate. At the same time, there exists a hydrophobic region for the binding of the acyl fragment of the substrate in the active site of BChE.The effective hydrolysis of the esters of propionic and butyric acids as well as the practical lack of stereoselectivity towards phosphororganic inhibitors with the asymmetric atom of phosphorus (cf. review[13]) can be explained with the influence of the latter.

As to the plot of pK_D vs. n (Fig. 1A and 1B), these data characterize the surroundings of the "binding place" of the ammonium ion in the active center of the enzyme. In connection with the flexibility of the polymethylene chain,

it is difficult to compare these data with a certain hydrophobic area observed around the esteratic or anionic centers of the enzymes[14].

Thus, the data obtained give evidence about the fact that there are clear differences between the active centers of AChE and BChE. These differences consist of the following: the efficacy of binding is determined by the different parts of the ligand molecule



AChE is sensitive to the hydrophobicity of the group - N^{+} - R, BChE interacts with the whole ligand molecule.

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QUANTITATIVE STATISTICAL INTERPRETATION OF KINETIC DATA IN THE GAS PHASE HOMOLYSIS
7. Recalculation of Conventional Heats of Formation and Entropies of Free Radicals in Transition State

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A more comprehensive set of experimental kinetic parameters reported in literature for reactions of the gas phase homolysis has been processed. The formal isokinetic dependence in the coordinates $\log k_T - \log k_{T_2}$ has been proved. The results of the calculation[1,2] of the conventional heats of formation at 0 and 298 K and entropies for free radicals in the transition state obtained within the framework of the iterative procedure as well as the conventional heats of formation proceeding from the isoentropic model at 0 and 298 K are presented.

Characteristics of the Data Used

In our previous papers[1-7] of this series, a detailed representation of the results of the quantitative interpretation, within the framework of the formal approach of the kinetic data for the gas phase unimolecular homolysis according to the scheme:

$$R_i - R_j \rightarrow R_i\cdot + R_j\cdot \qquad (1)$$

has been carried out. The values of experimental activation parameters used were mainly extracted from the tables of V.I. Vedeneev and A. A. Kibkalo[8], and also completed by some more recent data. Statistically and for purely calculation purposes, it was reasonable to consider the present type of reactions as an isoentropic case where the variance of activation entropy occurs as a result of random deviations. An attempt to establish the presence and values of possible real variation in the activation entropy dependent on the nature of radicals showed[7] that the values of entropies of activation $\Delta S_R^{\neq}$. for a large number of radicals remained sufficiently unreliable because of the lack and unreliability of the corresponding experimental data. Thus, taking into account the new experimental kinetic data on the gas phase homolysis as well as the improved possibilities of the computer ("ND - 100") being at our disposal, it is of interest to make the statistical treatment of an approximately twice increased quantity of initial information on the kinetics of the gas phase homolysis within the framework of the models described earlier[1-7]. The set of literature data processed in this work comprises publications prior to the beginning of 1985. A full list of formed free radicals and the substituents corresponding to them in initial compounds included in this work is represented in Table 1. Radicals-substituents with sequence numbers (indexes) 1-189 correspond to those listed in Table 1 of Ref. 4, hydrogen has new index 190 (instead of 0 in paper[4]) and the groups which did not occur earlier[1-7] have numbers 191-267. New initial experimental data for the homolyzing compounds R_iR_j are listed in Table 2 in the form which is analogous to that of Ref. 4.

At the present time this table is probably a fairly full compilation of the experimental values of the Arrhenius parameters of the gas phase homolysis, completing the data in the monographs[10,8]. In Table 2, the following values are listed after no. : indexes i and j for departing groups R_i and R_j; statistical factor indicating a number of equivalent bonds undergoing the homolysis; values of lower and upper limits of experimental temperatures in K; activation para-

meters log A (A in sec^{-1}) and E (kcal/mole) from Arrhenius equation; number of order of literature source for reported values of log A and E; heats of formation of initial compounds R_iR_j ΔH^o_{f0} at 0 K and ΔH^o_{f298} at 298.15 K; number of order for literature source of ΔH^o_{f298} (and ΔH^o_{f0}); value of interaction energy between R_i and R_j in compound R_iR_j within the framework of calculation scheme for heats of formation of organic compounds (see [1,4-7]); an auxiliary character constant (see below), and experimental method of determination of kinetic parameters.

The data from Table 2 of paper[4] were also included into the initial set for statistical processing with the exception of lines 7, 21, 28-30, 32, 43-44, 66, 77, 103-106, 119-122, 168, 171, 267, 299, and 417 - 432, rejected preliminarily as unreliable or being pure estimations. The data belonging to the fall-off region have been retained among the included initial kinetic parameters. However, the comparison of available parallel data for some reactions indicates the absence of essential differences between the values of high-pressure and fall-off regions (see, for example, kinetic parameters for the homolysis of ethane in book[8]). For the preliminary selection of the initial data we have introduced an auxiliary sign - character constant consisting of two symbols. The latter have the following meanings:

Position	Symbol	Meaning
1	A	There has been a single sufficiently precise or only single value for the formation heat of homolyzing compound $\Delta H^o_{fR_iR_j}$
1	B	Alternative values of $\Delta H^o_{fR_iR_j}$ are reported in literature
2	A	Kinetic data for high-pressure limit
2	B	Kinetic data for fall-off region and other less reliable values

This sign was used for the automatic preliminary selection of either the total set available or the special set referring more strictly to the high-pressure limit. Moreover, in the first cycle of iteration starting from the literature values of log A^{7}, where entropies of activation for radicals $\Delta S^{\neq}_{R\cdot}$ were calculated, the preliminary exclusion of the lines, corresponding to the alternative heats of formation of initial compounds, was carried out.

The first 23 lines of Table 2 correspond to the data from the monograph of S.W. Benson and H.E. O'Neal and are cited according to this source. Further the data are mainly listed in the next order of homolyzing bonds: C-H, N-H, C-C, C-Hal, N-N, C-N (except NO_2), C-NO_2, N-O, N-NO_2, O-O, X-O, C-S, the rest of C-X, where X denotes a group whose first atom is a heteroatom. Besides, the kinetic parameters of reactions for which we could not find the heats of formation of reagents in literature (it was also impossible to calculate the values of the interaction energies in their case) are reported at the end of Table 2.

Temperature Dependence on Heats of Formation of Free Radicals

One can express the activation energy for the reactions of the gas phase homolysis (1) at temperature T by the following equation[1,4] (assuming the absence of interaction between the free radicals formed) :

$$D(T) = \Delta H^{\neq}_{R_i\cdot}(T) + \Delta H^{\neq}_{R_j\cdot}(T) - \Delta H^{o}_{fR_iR_j}(T) \qquad (2)$$

where $\Delta H^{\neq}_{R\cdot}(T)$ denote the heats of formation of free radicals in the transition state, and $\Delta H^{o}_{fR_iR_j}(T)$ - the heat of formation of the reagent R_iR_j at temperature T. In the previous publications[1-7], the additivity of temperature-contributions of enthalpies during the transition state was also suggested:

$$(H_T^o - H_O^o)_{R_i\cdot}^{\neq} + (H_T^o - H_O^o)_{R_j\cdot}^{\neq} = (H_T^o - H_O^o)_{R_iR_j} \qquad (3)$$

Then the D(0) value is expressed as follows:

$$D(0) = \Delta H_{R_i\cdot}^{\neq} + \Delta H_{R_j\cdot}^{\neq} - \Delta H_{fOR_iR_j}^o \qquad (4)$$

where $\Delta H_{R\cdot}^{\neq}$ denote the conventional heats of formation of free radicals in the transition state at 0 K, is $\Delta H_{fOR_iR_j}^o$ the standard heat of formation of the compound R_iR_j in the gas phase at 0 K. The latter ones were mainly estimated from the ΔH_{f298}^o values, using the technique described in Ref.2. It is clear that the ΔH_{f298}^o values are more reliable compared with ΔH_{fO}^o. Consequently the application of the ΔH_{f298}^o values is quite justified. Eq. (4) may be transformed as follows:

$$D(298) = \Delta H_{R_i\cdot}^{\neq} + \Delta H_{R_j\cdot}^{\neq} - \Delta H_{f298\ R_iR_j}^o \qquad (5)$$

where $\Delta H_{R_i\cdot}^{\neq}$ denotes the conventional heats of formation of free radicals in the transition state at 298.15 K and $\Delta H_{f298R_iR_j}^o$ is the standard heat of formation of the compound R_iR_j in the gas phase at 298.15 K. For the temperature-contributions of the activation enthalpy the following additivity is assumed in this case :

$$(H_T^o - H_{298}^o)_{R_i\cdot}^{\neq} + (H_T^o - H_{298}^o)_{R_j\cdot}^{\neq} = (H_T^o - H_{298}^o)_{R_iR_j} \qquad (6)$$

The comparison of Eqs. (3) and (6) leads to a logical assumption that Eq. (6) is more valid as far as the difference of temperatures T-298 is less than T-0. One can compare, for example, the $(H_T^o - H_{298}^o)$ and $(H_T^o - H_O^o)$ values for the compounds R_iR_j obtained from sums $(H_T^o - H_{298}^o)_{R_i} + (H_T^o - H_{298}^o)_{R_j}$

and $(H_T^o - H_0^o)_{R_i}$ + $(H_T^o - H_0^o)_{R_j}$ with literature values $(H_T^o - H_{298})_{R_iR_j}$ and $(H_T^o - H_0^o)_{R_iR_j}$. Using the $(H_{800}^o - H_{298}^o)$ and $(H_{800}^o - H_0^o)$ values (in kcal/mole) from the monograph[9] for H(2.5 and 4.0), CH_3 (5.1 and 7.5), NO_2 (5.3 and 7.8) and NO_3 (7.6 and 10.2) the following results were obtained:

$$R_i\text{-}R_j \quad (H_{800}^o - H_{298}^o)_{R_iR_j} \quad (H_{800}^o - H_{298}^o)_{R_i} + (H_{800}^o - H_0^o)_{R_iR_j} \quad (H_{800}^o - H_0^o)_{R_i} +$$

$$+ (H_{800}^o - H_{298}^o)_{R_j} \qquad + (H_{800}^o - H_0^o)_{R_j}$$

CH_3- H	5.9	7.6	8.3	11.5
CH_3- CH_3	9.9	10.2	12.8	15.0
CH_3- NO_2	10.2	10.4	13.3	15.3
NO_3- NO_2	14.7	12.9	18.9	18.0

One can see that assumption (6) is really more strictly valid compared with Eq.(3). However, it must be taken into consideration that these are only single patterns, connected with the temperature-contributions of enthalpies for the isolated particles. Consequently, it is reasonable to use the ΔH_{f298}^o values instead of the ΔH_{f0}^o ones in case of the statistical treatment of the kinetic data on the gas phase homolysis.

Results and Discussion

In addition to Table 2, the data from Table 2 of Ref. 4 (except for the lines mentioned above) served as the file of the initial data for the statistical treatment.

Previously the isokinetic relationship was tested in the coordinates of $\log k_{T_2}$ and $\log k_{T_1}$ (see paper[3]):

$$\log k_{T_2} = a + \alpha \log k_{T_1} \tag{7}$$

where

$$\alpha = (T_2 - \beta)T_1/(T_1 - \beta)T_2 \tag{8}$$

$$a = \log A_o(1 - \alpha) \tag{9}$$

β - is the isokinetic temperature.

The data treatment was performed by means of a computer ND-100 using a program for the linear regression analysis with the automatic exclusion of the lines according to the Student's criterion. The total set comprising all the available data as well as the separate subset belonging to the high-pressure limit (the lines with the character AA in Table 2) were processed. The temperatures T_1 and T_2 were calculated either as the mean values of the corresponding lower and upper limits of the experimental temperatures or the other values were arbitarily put in.

The results of the statistical data treatment in the coordinates of Eq. (7) are reported in Table 3. 696 independent pairs of log k_{T_1} and log k_{T_2} estimates were covered by the total data set from which 338 lines were listed in publication[4] and 358 lines are from Table 2 (characterized by AA and AB). The set for the high-pressure limit covered 498 lines having characters AA in Table 2.

In all cases the slope α is indistinguishable from the ratio of T_1/T_2. Therefore, one can confirm the conclusion that the reactions of the unimolecular gas phase homolysis belong formally to the isoentropic series with the constant effective value of the preexponential factor. It means the mutual independence of the structural effects influencing the log A and E, besides the dependence of log k on the structure is mainly determined by the corresponding changes in the E values . If in paper[3] for the effective mean preexponential factor the value of 14.64 ± 0.04 was obtained, for the total data set this is higher. The data for the high-pressure limit lead to some more higher value as it is expected.

One can estimate also the variation of the log A values analogously to that in Ref. 3. Assuming that true deviations Δ make a contribution equalling $\Delta_{mean}(1 - \alpha)$, to the value s, where Δ_{mean} is the square-root mean value of Δ, then from the values s = 0.21 (T_1 = 766.6 and T_2 = 907.8) and s = 0.17 (T_1 = 700 and T_2 = 800) Δ_{mean} = 1.4 is derived. From the values s = 0.16 (T_1 = 786.5 and T_2 = 944.2) and

and s = 0.12 (T_1 = 700 and T_2= 800) for the data of the high-pressure limit Δ_{mean} = 1.0 is obtained (see Table 3). Hence, for the total data set 2/3 of all log A values are placed in the range from 13.8 to 16.6 and 95% in the range from 12.4 to 18. 2/3 values of log A for the data of the high-pressure limit are within 14.8 to 16.8 and 95% within 13.8 to 17.8.

Further one can estimate the degree of adequacy for the calculation scheme based on the neglection of the real variation of the log A values. The estimation of the upper limit of the standard error SMX for this scheme according to the equation[3]:

$$SMX = 2.3RT\ \Delta_{mean} \cdot 10^{-3}\ \text{kcal/mole}$$

leads to the values 5.3 kcal/mole (T = 837 K) for the total data set and 3.9 kcal/mole (T=865 K) for the data of the high-pressure limit.These values are lower than SMX=6 kcal/mole obtained in Ref.3.Taking into account experimental errors in the log k values,the variation of log A values gives an essentially smaller contribution into the standard deviation of the calculation scheme which describes the gas phase homolysis[3-4].

Among different models tested[1,3-7] for the investigation of structural effects on the log A and E values, the model with independent enthalpy and entropy contributions calculated by means of the iterative procedure[7] seems to be the most hopeful and reflects the reality more accurately. The effective $\Delta H^{\neq}_{R\cdot}$ and $\Delta\Delta H^{\neq}_{R\cdot}$ values were estimated using multilinear regression analysis (MLRA) according to equations:

$$\Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot} = E_{ij} - RT_{mean} + \Delta H^{o}_{fR_iR_j} \qquad (10)$$

$$\Delta\Delta H^{\neq}_{R_i\cdot} + \Delta\Delta H^{\neq}_{R_j\cdot} = E_{ij} - RT_{mean} + I_{R_iR_j} \qquad (11)$$

where $\Delta H^{\neq}_{R\cdot}$ are the conventional heats of formation of the free radicals in the transition state to be determined at 0 K, E_{ij} is the energy of activation, R is the universal gas constant, and T_{mean} is the mean absolute temperature for

the given pair of the Arrhenius parameters of log A_{ij} and E_{ij}. In Eq. (11) the $\Delta\Delta H^{\neq}_{R\cdot}$ values are the differences between the heat of formation of free radical and the additive term for the corresponding substituent:

$$\Delta\Delta H^{\neq}_{R_i\cdot} = \Delta H^{\neq}_{R_i\cdot} - \Delta H^{o}_{fR_i} -$$

$$\Delta\Delta H^{\neq}_{R_j\cdot} = \Delta H^{\neq}_{R_j\cdot} - \Delta H^{o}_{fR_j} -$$

and $I_{R_iR_j}$ is the term of the interaction energy between substituents R_i and R_j. The entropies of free radicals $\Delta S^{\neq}_{R\cdot}$ in the transition state were also estimated resulting in the MLRA procedure in coordinates of equation:

$$\Delta S^{\neq}_{R_i\cdot} + \Delta S^{\neq}_{R_j\cdot} = 2.3R\,(\log A_{ij} - \log n_{ij} - \log(ek'T_{mean}/h)) \qquad (12)$$

in which A_{ij} is the preexponential factor, n_{ij} is the statistical factor, k' denotes the Boltzmann and h - the Planck constant.

The iterative procedure started either from the literature experimental log A or E values and these two versions were marked as procedures A) and B), respectively.

Therefore we have composed the program HOMIT in FORTRAN for a computer ND-100, enabling the realization of the described iterative procedure[1,7]. The program permits also to calculate the conventional heats of free radicals in the transition state within the framework of the isoentropic model while the constant value of either log A_o or $\Delta S^{\neq}$ is fixed previously or that is included into the parameters to be determined during the MLRA.

Different possibilities are taken into consideration in the program HOMIT for the iterative procedure, particularly the treatment may occur at different minimum numbers of reactions and lines for each of the radicals included into the MLRA; the treatment of the total data set or only the data more strictly belonging to the high-pressure limit, the fixed values of $\Delta H^{\neq}_{R\cdot}$ ($\Delta\Delta H^{\neq}_{R\cdot}$) and $\Delta S^{\neq}_{R\cdot}$ for some radi-

cals-substituents may be used, exclusion of significantly deviating lines according to the Student's criterion at different confidence levels, using the values of ΔH^{o}_{f0}, ΔH^{o}_{f298} or interaction energies $I_{R_i R_j}$ as the heats of formation of reagents, reinclusion of the excluded lines before each cycle of the MLRA or not, etc.

In papers[1,3-7], the statistical treatment was mainly carried out for 13-15 of the most represented radicals. The radicals represented at least in two-lines of the initial data set were covered by the analysis using the HOMIT program. Inclusion of radicals occuring in single combinations does not increase the number of statistical degrees of freedom. For the previous data selection, the minimum numbers of reactions (NRN) and lines (NE) were assigned. The radicals--substituents characterized by these values were excluded from the set under processing .

Among the heats of formation in the gas phase for the groups listed in Table 1, the most reliable values are evidently those for the atoms H, F, Cl, Br, and I[266]. Although these values are the standard heats of formation for the isolated particles and in the present study the conventional heats of formation in the transition state are calculated, one can assume the agreement of those values. Inclusion of the $\Delta H^{\neq}_{R}$. values for the indicated five atoms into the unknown parameters led to the deviations of the obtained results comparing with the values calculated from the dissociation energies for the corresponding diatomic molecules[266]. Thus, it is reasonable to fix previously the $\Delta H^{\neq}_{R}$. values for the mentioned five atoms at the levels based on the dissociation energies of the diatomic molecules.

It was observed in paper[7] that the $\Delta S^{\neq}_{R}$. values for atoms of hydrogen, chlorine, bromine and iodine may be equalled to zero. If the $\Delta S^{\neq}_{R}$. values for the indicated atoms as well as those for F are included into the unknown parameters, the following results are obtained: $\Delta S^{\neq}_{F}$. ≈7, $\Delta S^{\neq}_{Br}$. ≈ ≈−7, and for other atoms $\Delta S^{\neq}_{R}$. = 0 entropic units. At that one must take into consideration a large uncertainty of the $\Delta S^{\neq}_{R}$. values. Thus, for example, data processing of the

total data set in the coordinates of Eq. (12) leads to the normalised standard deviation $s_o = 0.87$, after the exclusion of significantly deviating points at confidence level 0.95, $s_o = 0.53$. Therefore we consider the previous assignment $\Delta S^{\neq}_{R\cdot} = 0$ for hydrogen and halogen atoms to be quite justified .

The use of the above-mentioned iterative procedure in Ref. 7 was caused by the impossibility of the simultaneous accurate determination of the entropy and enthalpy contributions in the free activation energy. This was expressed by a significant overpumping effect and improbable $\Delta H^{\neq}_{R\cdot}$ and $\Delta S^{\neq}_{R\cdot}$ values for a great number of radicals. Despite a considerably expanded set of radicals used in this communication, the iterative procedure leads also to the improbable $\Delta H^{\neq}_{R\cdot}$ and $\Delta S^{\neq}_{R\cdot}$ values for some radicals with contradictory kinetic parameters if the excluded lines are reincluded after each MLRA cycle (the iteration in article[7] was carried out like this). Therefore, in the given communication the lines excluded during the MLRA was not taken into account in the following stages. In order to obtain a lower risk level for the exclusion of reliable data in the first MLRA cycles already, the method of gradual decreasing of the confidence level, in the course of which the markedly deviating lines were excluded according to the Student's test, was chosen. The zero-order approximations of the $\Delta S^{\neq}_{R\cdot}$ and $\Delta H^{\neq}_{R\cdot}$ or $\Delta\Delta H^{\neq}_{R\cdot}$ values were calculated after the exclusion of lines on the confidence level of 0.99, the first approximations on the level of 0.98 etc. up to the value 0.95 as the most frequently used one for the fourth-order approximations.

The results obtained using the iterative procedures A) and B) according to Eqs. (10) - (12) and also within the framework of the isoentropic model excluding the markedly deviating lines according to the Student's criterion on the confidence level 0.95 using equations:

$$\Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot} = E_{ij} + \Delta H^{o}_{fR_iR_j} + \Delta S^{\neq}T_{mean}/10^3 + \\ + 2.3RT/_{mean}(\log k'T_{mean}/h + \log n_{ij} - \log A_{ij}) \qquad (13)$$

and

$$\Delta\Delta H^{\neq}_{R_i\cdot} + \Delta\Delta H^{\neq}_{R_j\cdot} = E_{ij} + I_{R_iR_j} + \Delta S^{\neq}_{T_{mean}} / 10^3 +$$

$$+ 2.3RT_{mean}(\log k'T_{mean} / h + \log n_{ij} - \log A_{ij}) \quad (14)$$

are listed in Tables 1,4, and 5. There are the final values of the conventional heats of formation $\Delta H^{\neq}_{R\cdot}$ for the free radicals in the transition state at 0 and 298 K and the $\Delta\Delta H^{\neq}_{R\cdot}$ values for nine different variants in Table 1. In the last three columns of Table 1 the entropies of the free radicals in the transition state $\Delta S^{\neq}_{R\cdot}$, corresponding to the $\Delta H^{\neq}_{R\cdot}$ and $\Delta\Delta H^{\neq}_{R\cdot}$ values of variants 1, 2, and 7, are listed. The $\Delta S^{\neq}_{R\cdot}$ values obtained using the formation heats of reagents at 298 K,are very close to the respective $\Delta S^{\neq}_{R\cdot}$ values,related to the $\Delta H^{\neq}_{R\cdot}$ values at 0 K.The iterative procedures A) and B) for Eqs. (11) and (12) lead also to similar $\Delta S^{\neq}_{R\cdot}$ values. Therefore, the $\Delta S^{\neq}_{R\cdot}$ values for procedure B) are reported in Table 1 only.

At the end of Table 1, the normalized standard deviation (s_o), standard deviation (s), the number of lines (NE), the number of reactions (NRN), and the constant value of activation entropy (in the case of isoentropic model) are listed for each variant of treatment after five iteration cycles (ten stages of MLRA) and exclusion of significantly deviating points according to the above-mentioned method. The value $\Delta S^{\neq}_{const} = 9.8$ entr. un. corresponds to $\log A_o = 15.82$, obtained by the treatment in the coordinates of the isokinetic relationship $\log k_{T_2} - \log k_{T_1}$ using the data of the high-pressure limit (see Table 3).[1] As regards the uncertainties of the $\Delta H^{\neq}_{R\cdot}$, $\Delta\Delta H^{\neq}_{R\cdot}$, and $\Delta S^{\neq}_{R\cdot}$ values, one can see that the standard deviations for the indicated values are not higher than 0.4 kcal/mole and 0.5 entr. un. for versions 1, 2, 4, 5, 10, and 11. For other variants (3, 6-9,12),maximum limits achieve 1.1 kcal/mole and 0.8 entr. un.. Real deviations of the calculated $\Delta H^{\neq}_{R\cdot}$, $\Delta\Delta H^{\neq}_{R\cdot}$, and $\Delta S^{\neq}_{R\cdot}$ values must be higher. Discrepancies between the corresponding val-

ues obtained in the result of the iterative procedures A) and B) may serve as direct indications of this. These deviations in case of the radicals occuring more seldom may be several kcal/mole or entr. un. and for the radical no. 254 ($3\text{-}NH_2\text{-}C_6H_4$) the $\Delta H^{\neq}_{R\cdot}$ values of variants 1 and 2 differ by 29.3 kcal/mol and the $\Delta S^{\neq}_{R\cdot}$ values of variants 9 and 10 by 32.1 entr. un.. However, these differences can be simply explained,whereas for the given radical some contradictory alternative data are available.The log A values 17.5 and 10.55 E values 72.0 and 43.0 kcal/mole are listed for the bond fission reaction of $3\text{-}NH_2\text{-}C_6H_4\text{-}NO_2$ (see Table 2).Using the iterative procedure B), the line with parameters log A= =17.5 and E=72.0 is excluded and the $\Delta H^{\neq}_{3\text{-}NH_2\text{-}C_6H_4\cdot}$ and $\Delta S^{\neq}_{3\text{-}NH_2\text{-}C_6H_4\cdot}$ values have been calculated from the parameters log A=10.55 and E=43.0.In case of the Procedure A),it ie vice versa.This example gives a clear advantage to the procedure A) but in general,it is hard to prefer any of the used iterative procedures.One can attempt to draw some more definite conclusions proceeding from the examination of the substituent effects in the $\Delta H^{\neq}_{R\cdot}$, $\Delta\Delta H^{\neq}_{R\cdot}$, and $\Delta S^{\neq}_{R\cdot}$ values for different types of free radicals,e.g.$X^1X^2X^3C\cdot$, $XO\cdot$, $X^1X^2N\cdot$ etc. However, this goes out of the limits of the present communication.

In Table 4, all nine variants from Table 1 have been given a more detailed characterization indicating the numbers of the included lines and reactions, s_o, and s. In Table 5, the coded list of reactions and the numbers of lines for these reactions after each MLRA cycle for version 1 of Table 1 are presented.

The results obtained in Tables 1-5 confirm a low degree of accuracy of deecription within the models used by us when the total available data set of the kinetic parameters for the gas phase homolysis is used (before exclusion of the markedly deviating lines). However, one must remember large uncertainties in initial experimental data which are expressed by significant scattering of alternative values for separate reactions[1,10]. More reliable description is inevitably con-

nected with the exclusion of significantly deviating lines. At the same time, the exclusion of the alternative data retaining the total number of different reactions is desirable. One can see in Table 4 that in the course of the exclusion of significantly deviating lines the decrease of the number of the included reactions is slower compared with the number of the included lines, i.e. the predominant majority of reactions are not excluded but the number of lines may be decreased more than twice (variants 1, 2, 4, and 5). At that it is hard to decide up to which approximation the iterative procedure should be continued. The $\Delta H^{\neq}_{R\bullet}$ and $\Delta S^{\neq}_{R\bullet}$ values of the fourth approximation obtained on the confidence level 0.95 permit to calculate the log k values for the gas phase homolysis more accurately, comparing with those found from the experimental Arrhenius parameters for separate reactions. For example, assuming that the deviations are 0.2 kcal/mole and 0.2 entr. un. for the $\Delta H^{\neq}_{R\bullet}$ and $\Delta S^{\neq}_{R\bullet}$ the estimated uncertainty for the calculated log k value at 800 K according to equation:

$$s_{\log k}=\sqrt{\left(\sqrt{s^2_{\Delta S^{\neq}_{R_i\bullet}}+s^2_{\Delta S^{\neq}_{R_j\bullet}}}/2.3R\right)^2+\left(\sqrt{s^2_{\Delta H^{\neq}_{R_i\bullet}}+s^2_{\Delta H^{\neq}_{R_j\bullet}}}/2.3RT\right)^2}$$

is equal to 0.1. In Ref. 1, for the homolysis of ethane with the formation of two methyl radicals the log k values are calculated at three temperatures proceeding from the five mutually most consistent sources of experimental data. Inaccuracies of the log k values are at that ranged within the limits of 0.12 - 0.25. It must also be mentioned that despite possible significant discrepancies in the $\Delta H^{\neq}_{R\bullet}$, $\Delta\Delta H^{\neq}_{R\bullet}$, and $\Delta S^{\neq}_{R\bullet}$ values obtained in result of the iterative procedures A) and B) (see Table 1), the log k values calculated proceeding from them are in good agreement. For example, the iterative procedure A) leads to the $\Delta H^{\neq}_{R\bullet}$ and $\Delta S^{\neq}_{R\bullet}$ values of 40.0 kcal/mole and 0.8 entr. un. for the

$\cdot NH_2$ radical and the procedure B) gives 37.9 kcal/mole and -1.2 entr. un. (see Table 1). Within the framework of the transition state theory, the log k value for the homolysis may be calculated by the equation:

$$\log k = \log (k'T/h) + (\Delta S^{\neq}_{R_i\cdot} + \Delta S^{\neq}_{R_j\cdot})/2.3R -$$

$$- (\Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot} - \Delta H^{o}_{fR_iR_j})/2.3RT \qquad (15)$$

The log k values calculated for the hydrazine (H_2N-NH_2) homolysis at 1000 K equal 1.90 and 1.95, respectively, according to the results of the A) and B) procedures. In Table 2, the values of log A = 13.9 and E = 55 kcal/mole lead to log $k_{1000\ K}$ = 1.88 and log $k_{1000\ K}$=2.02 corresponds to the values log A = 13.6 and E = 53 kcal/mole. Comparing the results obtained using the formation heats of reagents R_iR_j at 0 K with those at 298 K (see Table 4, variants 1, 2 and 4, 5), it may be seen that fitting accuracies characterized by the respective values of s and s_o are very close (at the same numbers of included lines). Thus, using the ΔH^{o}_{f298} values instead of ΔH^{o}_{f0}, the improvement of the reliability of description is not observed within the framework of the present approach. However, the scheme with the ΔH^{o}_{f298} values is preferable because the heats of formation at 298 K are more obtainable.

All the reactions of the gas phase homolysis examined in the present study may be roughly divided into three groups: fission of C-C, C-X, and X-X bonds where X denotes the radical-substituent in which the first atom is a heteroatom. All three indicated groups are represented in Table 1 (variants 1-6) where the experimental heats of formation of reagents are used. The calculation scheme[2] for the heats of formation of covalent compounds does not allow to include the reagents of type X-X as well as many compounds of type C-X to the variants 7-9, However, the number of C-C compounds is increased due to those whose experimental standard heats of formation we could

not find.

In Table 5, the dynamics of the included lines for different reactions at the first five approximations of the iterative procedure B) for version 1 is reflected. Out of 162 reactions 53 belong to the C-C type, 80 to the C-X, and 29 to the X-X. After the exclusion of significantly deviating lines at the level of the fourth-order approximation remain 43, 54, and 22 reactions, respectively. In case of all approximations (0 - 4), the contribution of the reactions involved is the largest for the homolysis of C-C type bonds, compared with the initial number of reactions. For the other types a more significant portion of the reactions is excluded. For the zero- and first-order approximations the relative number of the included C-X type reactions is somewhat higher comparing with the X-X type but for the second-, third-, and fourth-order approximations it is vice versa. As to the additivity rule, for both radicals R_i and R_j, it seems quite reasonable, whereas the constancy of bond breaking in the case of C-C bond fissions is valid. It should also be had in mind that the excluded reactions of the C-X and X-X type are mainly compounds consisting of small molecules, for example, C-H, C-Hal and other bond fissions. It is known that the experimental data for the pyrolysis of small molecules refer to a sufficiently low pressure, i.e. the fall-off region. Extrapolation to the high-pressure limit may be connected with considerable errors.

The conventional heats of formation of the $\Delta H^{\neq}_{R\cdot}$ ($\Delta\Delta H^{\neq}_{R\cdot}$) and $\Delta S^{\neq}_{R\cdot}$ entropies conjugated by them for free radicals in the transition state, as well as the formation heats obeying the isoentropic model, obtained in this investigation may be considered more reliable than those reported earlier[1-7]. Proceeding from the indicated values, one can estimate the rate constants of the gas phase homolysis according to Eq.(15) for all combinations of these radicals if the experimental value of $\Delta H^{o}_{fR_iR_j}$ at 0 or 298 K is known. If the calculation of the $I_{R_iR_j}$ value is possible, the estimation of the log k values is realized according to the following equation:

$$\log k = \log (k'T/h) + (\Delta S^{\neq}_{R_i\cdot} + \Delta S^{\neq}_{R_j\cdot})/2.3\ R -$$

$$- (\Delta\Delta H^{\neq}_{R_i\cdot} + \Delta\Delta H^{\neq}_{R_j\cdot} - I_{R_iR_j})/2.3\ RT\ , \qquad (16)$$

which is analogous to Eq. (15).

For the purpose of comparison, the results of the statistical treatment of the initial data more strictly related to the high-pressure limit are listed at the end of Table 4 (variant 10). One can see that higher reliability of description is achieved in case of a smaller number of radicals, reactions, and lines.

Table 1

List and Enumeration of Radicals-Substituents R• (R⁻) and Corresponding $\Delta H^{\neq}_{R\bullet}$, $\Delta\Delta H^{\neq}_{R\bullet}$ (in kcal/mole), and $\Delta S^{\neq}_{R\bullet}$ (in entr. un.) Valuee Obtained According to Eqs. (10) - (14)

s_o - normalized standard deviation

s - standard deviation in kcal/mole ($\Delta H^{\neq}_{R\bullet}$ and $\Delta\Delta H^{\neq}_{R\bullet}$) and in entr. un. ($\Delta S^{\neq}_{R\bullet}$)

NE - number of independent equations (lines)

NRN - number of different reactions (combinations of R_i and R_j)

$\Delta S^{\neq}_{const}$ - effective average value of activation entropy in entr. un.

Variants:

1) $\Delta H^{\neq}_{R\bullet}$ according to Eqs (10) and (12) for the iterative procedure B) at 0 K

2) The same by the iterative procedure A)

3) $\Delta H^{\neq}_{R\bullet}$ according to the isoentropic model by Eq. (13) at 0 K

4) $\Delta H^{\neq}_{R\bullet}$ analogously to variant 1) at 298 K

5) $\Delta H^{\neq}_{R\bullet}$ analogously to variant 2) at 298 K

6) $\Delta H^{\neq}_{R\bullet}$ according to the isoentropic model by Eq. (13) at 298 K

7) $\Delta\Delta H^{\neq}_{R\bullet}$ according to Eqs. (11) and (12) for the iterative procedure B)

8) $\Delta\Delta H^{\neq}_{R\bullet}$ analogously to variant 7) by the iterative procedure A)

9) $\Delta\Delta H^{\neq}_{R\bullet}$ according to the isoentropic model by Eq. (14)

10) $\Delta S^{\neq}_{R\bullet}$ related to the $\Delta H^{\neq}_{R\bullet}$ values of variant 1)

11) $\Delta S^{\neq}_{R\bullet}$ related to the $\Delta H^{\neq}_{R\bullet}$ values of variant 2)

12) $\Delta S^{\neq}_{R\bullet}$ related to the $\Delta H^{\neq}_{R\bullet}$ values of variant 7)

Table 1 continued

The data for the final set after the exclusion of significantly deviating lines according to Student's test on the confidence level 0.95 are listed. The $\Delta H_R^{\neq}$., $\Delta\Delta H_R^{\neq}$. and $\Delta S_R^{\neq}$. values for F, Cl, Br, I, and H are previously fixed at reported values.

No.	R	Variants											
		$\Delta H_R^{\neq}$.						$\Delta\Delta H_R^{\neq}$.			$\Delta S_R^{\neq}$.		
		1)	2)	3)	4)	5)	6)	7)	8)	9)	10)	11)	12)
1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	F	18.5	18.5	18.5	19.0	19.0	19.0	83.3	83.3	83.3	.0	.0	.0
2	CL	28.6	28.6	28.6	29.0	29.0	29.0	50.6	50.6	50.6	.0	.0	.0
3	BR	28.2	28.2	28.2	26.7	26.7	26.7	35.0	35.0	35.0	.0	.0	.0
4	I	25.6	25.6	25.6	25.5	25.5	25.5	18.7	18.7	18.7	.0	.0	.0
5	O	-	-	-	-	-	-	-	-	-	-	-	-
6	OH	10.6	7.2	12.8	9.7	6.0	9.6	63.7	62.0	64.0	3.9	.0	4.6
7	OF	28.0	28.6	28.2	27.3	27.5	27.8	-	-	-	3.7	4.4	-
8	OCL	-	-	-	-	-	-	-	-	-	-	-	-
9	CLOF	-	-	-	-	-	-	-	-	-	-	-	-
10	CLO2F	-	-	-	-	-	-	-	-	-	-	-	-
11	CLO3	-	-	-	-	-	-	-	-	-	-	-	-
12	CLO4	-	-	-	-	-	-	-	-	-	-	-	-
13	N2	-	-	-	-	-	-	-	-	-	-	-	-
14	NH2	37.9	40.0	44.0	36.1	37.5	42.8	47.0	49.1	53.6	-1.2	.8	-2.0
15	NF2	8.8	8.9	9.3	8.6	8.7	9.0	-	-	-	4.1	4.2	-

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
16	NO	21.4	20.6	21.6	20.8	20.1	21.0	-	-	-	4.8	4.2	-
17	NO2	7.6	7.0	7.9	6.5	6.2	6.5	27.2	26.6	30.0	4.7	4.0	2.0
18	ONO2	18.2	18.5	20.4	16.2	16.1	18.8	-	-	-	-3.4	-4.1	-
19	CO	-	-	-	-	-	-	-	-	-	-	-	-
20	CO2	-	-	-	-	-	-	-	-	-	-	-	-
21	SH	11.3	16.2	20.2	10 5	15.4	19.4	31.1	32.0	39.0	-5.6	.0	-4.5
22	SF5	-231.7	-231.7	-197.9	-235..	-235.4	-201.6	-	-	-	-8.5	-8.5	-
23	SO3F	-	-	-	-	-	-	-	-	-	-	-	-
24	OCH3	4.7	4.6	5.2	2.5	2.0	2.7	54.4	54.6	55.5	3.6	3.3	3.9
25	OCF3	-156.8	-156.9	-154.6	-159.4	-159.5	-157.2	-	-	-	5.1	5.1	-
26	OC2H5	-3.8	-3.2	-1.7	-7.4	-6.8	-5.2	55.7	55.6	59.2	.0	1.0	.0
27	OC3H7	-10.3	-9.4	-7.1	-14.2	-14.4	-12.0	-	-	-	-.9	.0	-
28	OCH(CH3)2	-7.8	-6.7	-9.6	-13.1	-12.0	-14.6	-	-	-	7.1	8.4	-
29	OC4H9	-9.6	-8.8	-12.2	-15.9	-15.3	-18.5	-	-	-	8.5	9.2	-
30	OC(CH3)3	-15.4	-15.3	-15.5	-22.5	-22.4	-22.6	-	-	-	5.2	5.3	-
31	OC(CH3)2C2H5	-19.1	-18.3	-20.8	-27.1	-26.4	-28.8	-	-	-	8.6	9.2	-
32	OCH=CH2	12.8	13.8	12.5	10.7	11.6	10.9	-	-	-	5.7	6.8	-
33	OCH(CH2ONO2)2	-	-	-	-	-	-	-	-	-	-	-	-
34	OCOCH3	-	-	-	-	-	-	-	-	-	-	-	-
35	OCOC2H5	-	-	-	-	-	-	-	-	-	-	-	-
36	OCOC3H7	-	-	-	-	-	-	-	-	-	-	-	-
37	OCOC6H5	-	-	-	-	-	-	-	-	-	-	-	-
38	OC6H5	9.8	11.3	15.3	6.2	5.9	12.4	36.9	35.5	41.9	.0	1.6	-1.8
39	NHCH3	40.1	38.0	42.3	36.8	35.4	38.4	47.4	47.3	52.3	-.7	-2.7	.0
40	NHC6H5	55.2	54.3	62.2	50.4	49.8	57.4	32.4	32.4	36.9	-3.3	-4.4	.8
41	N(CH3)2	36.8	36.6	39.3	30.8	32.0	34.7	45.7	46.0	44.9	.0	.0	5.6
42	N(C2H5)2	-	-	-	-	-	-	-	-	-	-	-	-
43	N(CH3)C6H5	55.3	55.0	65.3	48.4	48.9	57.7	24.4	24.3	30.1	-4.0	-4.3	-.5
44	N=CHCH3	-	-	-	-	-	-	-	-	-	-	-	-

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
45	NNCH3	56.2	55.9	56.8	53.0	53.0	53.9	-	-	-	3.1	2.6	-
46	NNCD3	-	-	-	-	-	-	-	-	-	-	-	-
47	NNCF3	-	-	-	-	-	-	-	-	-	-	-	-
48	NNC2H5	-	-	-	-	-	-	-	-	-	-	-	-
49	NNC3H7	41.4	44.5	47.8	37.7	37.9	41.0	-	-	-	-3.4	-1.7	-
50	NNCH(CH3)2	48.9	53.4	45.3	43.0	48.0	39.4	-	-	-	-6.2	1.6	-
51	NNC4H9	-	-	-	-	-	-	-	-	-	-	-	-
52	NNCH(CH3)C2H5	-	-	-	-	-	-	-	-	-	-	-	-
53	NNC(CH3)3	32.6	32.4	32.7	25.7	25.5	25.9	-	-	-	6.6	6.4	-
54	NNCH2CH=CH2	-	-	-	-	-	-	-	-	-	-	-	-
55	NNN(CH3)2	-	-	-	-	-	-	-	-	-	-	-	-
56	NNN(C2H5)2	-	-	-	-	-	-	-	-	-	-	-	-
57	NOCH3	-	-	-	-	-	-	-	-	-	-	-	-
58	NOCH2CH(CH3)2	-	-	-	-	-	-	-	-	-	-	-	-
59	SCH3	12.0	12.0	16.4	10.1	10.1	14.2	32.4	32.4	36.7	.0	.0	.0
60	SC6H5	39.5	39.5	44.3	35.7	35.7	40.6	-	-	-	.0	.0	-
61	SO2CH3	-75.3	-75.2	-74.6	-80.1	-80.4	-76.9	-	-	-	2.7	2.5	-
62	SI(CH3)3	.0	-1.7	.0	-7.5	-8.5	-6.6	-	-	-	4.7	2.6	-
63	ZNCH3	33.2	33.5	50.5	30.0	31.3	46.8	-	-	-	-13.1	-12.7	-
64	CDCH3	41.7	41.3	53.6	39.6	39.0	52.2	-	-	-	-10.6	-11.2	-
65	HGCL	10.8	9.2	18.3	12.6	10.1	17.3	-	-	-	-6.5	-7.8	-
66	HGBR	23.3	20.4	23.2	22.0	19.5	21.8	-	-	-	.9	-1.8	-
67	HGCH3	45.2	45.3	52.1	42.4	43.2	49.2	-	-	-	-3.9	-3.8	-
68	HGC2H5	43.0	40.7	47.7	41.0	37.0	44.6	-	-	-	-2.1	-6.2	-
69	HGCH(CH3)2	37.7	36.4	38.8	32.9	32.1	34.0	-	-	-	4.0	1.9	-
70	HGCH=CH2	-	-	-	-	-	-	-	-	-	-	-	-
71	GA(CH3)2	-	-	-	-	-	-	-	-	-	-	-	-
72	IN(CH3)2	-	-	-	-	-	-	-	-	-	-	-	-
73	TL(CH3)2	-	-	-	-	-	-	-	-	-	-	-	-

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
74	SNCL2CH3	-17.7	-17.6	-7.0	-19.4	-19.3	-8.7	-	-	-	-7.2	-7.0	-
75	SN(CH3)3	27.6	26.9	35.0	22.7	21.3	28.1	-	-	-	-3.7	-4.5	-
76	PB(CH3)3	49.4	51.4	59.7	43.8	45.8	54.1	-	-	-	-9.5	-6.7	-
77	PB(C2H5)3	62.0	63.0	57.8	52.0	52.8	48.2	-	-	-	10.7	11.7	-
78	SB(CH3)2	-	-	-	-	-	-	-	-	-	-	-	-
79	BI(CH3)2	-	-	-	-	-	-	-	-	-	-	-	-
80	CH3	33.9	33.7	33.9	31.9	31.8	32.0	49.9	50.0	49.7	5.0	4.8	5.1
81	CD3	-	-	-	-	-	-	-	-	-	-	-	-
82	C2H5	27.5	26.5	27.2	24.5	23.7	23.8	43.7	43.9	43.8	5.0	4.0	4.5
83	C3H7	25.5	22.4	22.8	19.2	19.0	19.6	46.0	46.1	45.0	7.0	5.3	5.7
84	CH(CH3)2	21.3	21.6	19.2	16.4	16.3	14.4	41.2	41.3	39.5	6.5	6.9	6.3
85	C4H9	-	-	-	-	-	-	-	-	-	-	-	-
86	CH(CH3)C2H5	17.1	17.0	16.4	10.9	10.9	10.2	41.2	41.9	40.0	5.7	5.6	5.7
87	C(CH3)3	12.7	12.9	11.6	6.3	6.5	5.1	38.2	38.4	36.9	6.4	6.7	6.4
88	CH(CH3)CH(CH3)2	14.6	10.0	12.0	4.8	.0	4.1	42.4	37.6	40.1	7.1	12.2	6.9
89	C(CH3)2C2H5	9.6	9.9	9.5	.0	-.9	1.6	40.1	39.3	37.6	5.2	5.5	7.6
90	CH2CH=CH2	39.8	39.5	40.6	37.2	36.1	38.4	31.2	30.7	33.6	2.0	.6	2.0
91	CH2C(CH3)=CH3	27.3	29.2	35.7	20.4	24.0	30.2	32.5	29.2	34.7	.0	3.1	3.3
92	CH(CH3)CH=CH2	32.8	33.0	33.3	28.6	28.7	29.0	29.2	29.1	30.1	4.1	4.3	3.1
93	C(CH3)2CH=CH2	27.6	27.7	25.4	21.1	21.2	18.8	26.8	26.7	24.8	8.0	8.2	7.8
94	CH2CCH	83.3	82.9	82.8	82.8	81.2	80.9	34.5	35.2	36.8	5.6	4.6	4.0
95	CH2CL	22.3	22.3	33.5	20.4	20.4	31.6	41.9	41.9	53.2	-2.0	-2.0	-2.0
96	CH2BR	38.5	38.5	51.3	34.9	34.9	47.7	43.4	43.4	56.2	-3.4	-3.4	-3.4
97	CH2OCH3	-	-	-	-	-	-	38.3	38.6	39.4	-	-	3.5
98	CH2C(X)H	-	-	-	-	-	-	-	-	-	-	-	-
99	CH2CN	56.1	56.2	59.8	54.6	54.8	58.4	35.9	36.0	41.0	.0	.0	.0
100	CH2C6H5	49.4	49.8	53.2	44.8	44.8	48.6	33.2	32.8	36.8	.7	1.1	1.1
101	CH2(2-CH3-C6H4)	42.1	42.1	46.4	36.2	31.8	39.9	27.4	27.4	35.4	.0	.0	3.4
102	CH2(3-CH3-C6H4)	42.5	39.9	48.0	36.3	36.3	41.3	32.1	32.3	37.4	.0	2.2	.0

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
103	CH2(4-CH3-C6H4)	36.3	36.3	47.1	29.0	29.0	40.2	24.8	24.8	36.4	.0	.0	.0
104	CH2(1-C10H7)	62.9	62.9	68.4	60.3	56.6	61.8	28.8	29.0	34.2	.0	.0	.0
105	CH2(2-C10H7)	54.6	54.6	69.2	47.2	47.2	61.8	19.9	19.9	34.5	-4.8	-4.8	-4.8
106	2-CH2-C5H4N	50.8	50.8	66.0	45.0	45.0	60.2	30.0	30.3	38.3	-4.4	-4.4	3.3
107	3-CH2-C5H4N	53.6	53.6	68.8	47.7	47.7	62.9	32.2	29.9	37.9	-4.4	-4.4	.0
108	4-CH2-C5H4N	-	-	-	-	-	-	32.9	26.1	37.6	-	-	.0
109	CHCL2	13.4	13.4	23.2	12.1	12.1	21.9	34.6	34.6	44.4	-1.7	-1.7	-1.7
110	CHBR2	38.2	36.6	49.8	32.3	31.9	43.9	34.4	34.4	46.4	-3.9	-5.8	-2.3
111	CHFNO2	-	-	-	-	-	-	52.5	53.0	47.7	-	-	11.3
112	CH(NO2)2	38.7	39.3	38.6	33.3	33.6	33.5	49.4	49.9	46.7	4.7	5.4	7.3
113	CH(C6H5)2	-	-	-	-	-	-	24.5	19.1	31.5	-	-	-3.6
114	CF3	-116.8	-120.0	-119.6	-119.9	-121.0	-121.2	35.7	29.9	29.5	16.5	11.8	8.5
115	CCL3	16.0	16.3	14.8	15.2	15.2	13.9	38.7	40.0	36.8	7.4	7.9	7.4
116	CBR3	43.4	43.4	56.3	37.8	37.8	50.7	30.3	30.3	40.7	-7.6	-7.6	-4.2
117	CF2NF2	-62.0	-62.1	-61.6	-65.0	-65.1	-64.6	-	-	-	4.4	4.3	-
118	CF2NO2	-53.7	-53.1	-53.8	-56.5	-56.3	-56.3	45.9	46.4	43.2	4.7	5.4	7.4
119	CF(NF2)2	-4.7	-4.8	-6.0	-9.1	-9.2	-10.4	-	-	-	7.1	7.0	-
120	CFCLNO2	-	-	-	-	-	-	45.7	46.3	43.2	-	-	7.0
121	CFBRNO2	-	-	-	-	-	-	43.4	44.0	41.7	-	-	5.2
122	CFINO2	-	-	-	-	-	-	40.5	41.0	37.9	-	-	7.1
123	CF(NO2)2	.4	1.0	1.5	-9.8	-9.6	-8.4	55.1	55.7	53.7	2.1	2.8	4.8
124	CCL2NO2	-	-	-	-	-	-	39.0	39.6	37.2	-	-	5.3
125	CCL(NF2)2	-	-	-	-	-	-	-	-	-	-	-	-
126	CCL(NO2)2	38.3	38.9	38.4	34.4	34.7	34.9	49.2	49.7	46.8	4.0	4.7	6.7
127	CBR(NO2)2	48.2	48.8	47.7	42.5	42.8	42.3	48.5	49.1	45.4	5.6	6.3	8.3
128	CI(NO2)2	-	-	-	-	-	-	46.3	46.8	44.7	-	-	4.4
129	C(NF2)3	37.2	37.1	36.9	31.4	31.3	31.0	-	-	-	5.5	5.4	-
130	C(NO2)3	55.7	56.1	53.5	50.9	51.0	49.0	56.5	56.9	51.8	8.8	9.3	11.5
131	COOH	-	-	-	-	-	-	38.5	43.9	42.9	-	-	.0

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
132	C(O)CH3	-6.0	-5.0	-4.9	-7.9	-7.0	-6.6	41.7	43.7	43.9	3.3	4.6	2.8
133	C(O)CF3	-	-	-	-	-	-	-	-	-	-	-	-
134	C(O)C6H5	26.1	25.4	26.6	23.0	22.3	23.1	42.4	42.3	43.6	5.3	4.5	3.7
135	C(C6H5)3	108.1	108.1	105.6	92.7	92.7	90.2	29.5	29.5	27.0	12.4	12.4	12.4
136	CH2CH2CL	17.9	17.9	27.2	8.5	8.5	17.8	36.3	36.3	45.6	-4.0	-4.0	-4.0
137	CH(CH3)OH	-	-	-	-	-	-	39.7	39.5	39.0	-	-	5.3
138	CH(CH3)NO2	19.7	20.3	17.5	15.1	15.4	13.2	44.4	45.0	39.6	9.0	9.7	11.6
139	CH(CH3)C6H5	43.1	46.3	47.1	36.5	39.9	40.6	28.0	28.2	32.9	.0	4.0	.0
140	CCL2CH3	-	-	-	-	-	-	37.0	37.5	34.9	-	-	6.1
141	C(NO2)2CH3	28.6	29.2	25.9	23.2	23.5	20.8	49.5	50.0	44.2	10.4	11.1	13.0
142	CF(NO2)CH3	-	-	-	-	-	-	50.6	51.2	45.2	-	-	12.8
143	CCL(NO2)CH3	-	-	-	-	-	-	39.7	40.2	39.1	-	-	2.7
144	CBR(NO2)CH3	-	-	-	-	-	-	42.9	43.4	39.4	-	-	9.1
145	C(CH3)(CN)C6H5	-	-	-	-	-	-	11.5	11.5	26.5	-	-	-12.8
146	CF(NO2)CF(NO2)2	-	-	-	-	-	-	57.2	57.7	50.6	-	-	16.5
147	C(NO2)2CF(NO2)2	15.3	15.9	12.6	8.7	8.9	6.3	55.0	55.5	49.7	11.2	11.9	13.9
148	C(NO2)2C(NO2)3	73.5	74.1	71.3	65.5	65.7	63.6	55.5	56.0	50.8	9.9	10.6	12.6
149	CH(C2H5)NO2	18.6	19.2	15.9	12.8	13.1	10.4	45.7	46.2	40.5	7.9	12.2	12.4
150	C(CH3)2OH	-	-	-	-	-	-	36.6	36.5	36.8	-	-	4.8
151	C(CH3)2CN	41.1	41.1	46.0	36.6	36.6	41.5	28.4	28.6	33.4	.0	.0	.0
152	C(CH3)2NO2	18.0	18.6	12.1	12.1	12.4	6.5	46.6	47.2	38.1	17.2	17.9	19.8
153	CCL2C2H5	-	-	-	-	-	-	38.0	38.6	36.2	-	-	5.7
154	C(NO2)2C2H5	23.2	23.8	21.2	16.5	16.8	14.8	48.7	49.2	44.1	8.9	9.6	11.6
155	CH(NO2)C3H7	13.7	14.3	10.8	6.6	6.9	4.0	45.8	46.3	40.4	10.1	10.8	12.8
156	C(NO2)2C3H7	-	-	-	-	-	-	49.9	50.5	43.6	-	-	15.4
157	CH=CH2	59.6	59.7	57.9	57.8	58.0	56.1	51.5	51.3	49.2	5.9	5.9	5.9
158	C(CH3)=CH2	54.4	54.5	43.5	51.3	51.4	40.4	48.8	48.8	38.2	13.9	14.1	13.8
159	C(CF3)=CF2	-	-	-	-	-	-	-	-	-	-	-	-
160	C6H5	75.7	78.7	83.0	71.8	74.3	79.1	55.8	56.0	60.3	1.7	4.4	3.0

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
161	2-CL-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
162	3-CL-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
163	4-CL-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
164	2-NO2-C6H4	69.5	70.3	76.8	64.6	65.1	72.2	-	-	-	-6.8	-5.8	-
165	3-NO2-C6H4	64.4	71.5	74.6	59.2	66.3	68.8	-	-	-	-7.0	.0	-
166	4-NO2-C6H4	70.8	70.9	69.7	65.5	61.9	64.8	-	-	-	.0	.0	-
167	2-CH3-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
168	3-CH3-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
169	4-CH3-C6H4	64.9	59.2	63.1	58.2	54.2	59.0	31.6	33.2	49.7	7.2	.0	-8.8
170	2,5-(NO2)2-C6H3	-	-	-	-	-	-	-	-	-	-	-	-
171	2,6-(NO2)2-C6H3	-	-	-	-	-	-	-	-	-	-	-	-
172	3,5-(NO2)2-C6H3	77.5	77.7	80.8	71.9	72.1	77.0	-	-	-	.0	.0	-
173	2-CH3-5-NO2-C6H3	-	-	-	-	-	-	-	-	-	-	-	-
174	3-CH3-5-NO2-C6H3	-	-	-	-	-	-	-	-	-	-	-	-
175	4-CL-3,5-(NO2)2--C6H2	-	-	-	-	-	-	-	-	-	-	-	-
176	4-NH2-3,5-(NO2)2--C6H2	-	-	-	-	-	-	-	-	-	-	-	-
177	4-CH3-3,5-(NO2)2--C6H2	51.6	52.1	60.2	45.1	45.3	54.1	-	-	-	-9.9	-9.2	-
178	1-C10H7	66.6	67.6	75.8	61.4	62.3	71.1	-	-	-	-4.3	-3.3	-
179	2-C10H7	-	-	-	-	-	-	-	-	-	-	-	-
180	9-ANTHRYL	-	-	-	-	-	-	-	-	-	-	-	-
181	9-PHENANTHRYL	-	-	-	-	-	-	-	-	-	-	-	-
182	CH2F	-10.8	-7.6	-13.2	-10.4	-9.3	-14.3	47.6	53.4	48.6	-2.6	2.1	5.4
183	CH2I	-	-	-	-	-	-	-	-	-	-	-	-
184	CHF2	-	-	-	-	-	-	43.3	42.9	40.0	-	-	7.3
185	CN	-	-	-	-	-	-	-	-	-	-	-	-
186	CHFCL	-	-	-	-	-	-	-	-	-	-	-	-
187	CHFBR	-	-	-	-	-	-	-	-	-	-	-	-
188	CHFI	-	-	-	-	-	-	-	-	-	-	-	-
189	C6H11	-	-	-	-	-	-	39.9	39.7	39.3	-	-	5.1

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
190	H	51.6	51.6	51.6	52.1	52.1	52.1	51.6	51.6	51.6	.0	.0	.0
191	UF5	-461.5	-461.5	-460.0	-460.6	-460.6	-459.1	-	-	-	8.6	8.6	-
192	OCH(CH3)C2H5	-10.8	-10.0	-12.3	-17.2	-16.6	-18.7	-	-	-	8.1	8.7	-
193	OC(CH3)=CH2	1.1	1.3	1.9	-2.0	-1.9	-1.2	-	-	-	4.1	4.3	-
194	OC(CF3)3	-	-	-	-	-	-	-	-	-	-	-	-
195	OCOCF3	-	-	-	-	-	-	-	-	-	-	-	-
196	NNCH2CH(CH3)2	-	-	-	-	-	-	-	-	-	-	-	-
197	NNCH2C6H5	-	-	-	-	-	-	-	-	-	-	-	-
198	NNC6H5	-	-	-	-	-	-	-	-	-	-	-	-
199	SC(CH3)3	-5.8	-6.0	-7.1	-14.5	-12.5	-13.4	28.3	28.1	29.5	7.2	7.0	3.5
200	ZNC2H5	39.1	42.2	45.7	34.6	37.4	41.1	-	-	-	.0	.0	-
201	HGC3H7	39.3	41.0	40.9	37.6	34.7	34.4	-	-	-	4.5	4.0	-
202	HGC4H9	-	-	-	-	-	-	-	-	-	-	-	-
203	HGC6H5	91.6	86.6	85.1	88.2	85.7	80.0	-	-	-	7.4	2.5	-
204	BH3	-	-	-	-	-	-	-	-	-	-	-	-
205	PF3	-	-	-	-	-	-	-	-	-	-	-	-
206	GE(CH3)3	31.1	30.1	32.7	26.1	22.8	26.4	-	-	-	3.8	3.0	-
207	AS(CH3)2	-	-	-	-	-	-	-	-	-	-	-	-
208	AS(CF3)2	-	-	-	-	-	-	-	-	-	-	-	-
209	SN(C2H5)3	31.0	31.8	35.6	20.5	18.3	24.0	-	-	-	.0	.9	-
210	C2D5	-	-	-	-	-	-	-	-	-	-	-	-
211	CH2CH(CH3)2	-	-	-	-	-	-	47.7	47.2	45.1	-	-	6.5
212	CH2CH=CHCH=CH2	50.7	50.9	50.1	46.6	46.7	46.0	27.9	27.8	27.6	5.6	5.8	5.4
213	CH(CH=CH2)2	-	-	-	-	-	-	24.7	24.6	26.0	-	-	3.0
214	CH2CCCH3	72.0	72.2	71.7	69.3	69.4	68.9	34.6	34.8	35.2	5.1	5.3	4.7
215	C(CH3)2CCH	-	-	-	-	-	-	28.2	28.1	31.3	-	-	1.9
216	CH2NH2	32.5	32.5	33.4	29.5	29.5	30.4	35.3	35.4	36.4	4.0	4.0	3.8
217	CH2C(O)CH3	-5.8	-5.8	-6.0	-9.5	-9.5	-9.7	41.5	41.5	41.3	10.0	10.0	10.0
218	CH2(2-F-C6H4)	-	-	-	-	-	-	-	-	-	-	-	-

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
219	CH2(3-F-C6H4)	-	-	-	-	-	-	-	-	-	-	-	-
220	CH2(4-F-C6H4)	-5.9	-5.9	9.6	-10.8	-10.8	4.7	24.2	24.2	39.7	-4.4	-4.4	-4.4
221	CH2/2,5-(CH3)2-C6H3/	35.4	35.5	40.3	28.2	28.3	33.1	31.1	31.0	36.3	.5	.6	.3
222	CH2/2,6-(CH3)2-C6H3/	35.5	35.7	40.3	28.4	28.5	33.1	30.0	29.9	35.0	.5	.7	.3
223	CH2/3,5-(CH3)2-C6H3/	35.8	35.9	40.7	28.3	28.4	33.2	32.1	32.0	37.3	.5	.6	.3
224	CH2C6F5	-	-	-	-	-	-	-	-	-	-	-	-
225	CH2(9-ANTHRYL)	-	-	-	-	-	-	-	-	-	-	-	-
226	CHCLCH=CH2	-	-	-	-	-	-	32.5	32.4	27.3	-	-	11.3
227	CH(OH)CH=CH2	-	-	-	-	-	-	27.1	27.0	25.6	-	-	6.8
228	CHCLCF3	-	-	-	-	-	-	-	-	-	-	-	-
229	CF2	-	-	-	-	-	-	-	-	-	-	-	-
230	C(NO2)2SCH3	-	-	-	-	-	-	-	-	-	-	-	-
231	C(NO2)2SC6H5	-	-	-	-	-	-	-	-	-	-	-	-
232	C(NO2)2S /2,4-(NO2)2-C6H3/	-	-	-	-	-	-	-	-	-	-	-	-
233	CHO	8.6	7.9	7.1	8.6	7.4	6.8	48.1	46.3	45.9	5.5	5.1	6.5
234	COCH2C6H5	-	-	-	-	-	-	-	-	-	-	-	-
235	CH2CH2CN	58.4	58.6	57.1	55.9	56.0	54.5	43.4	43.3	42.4	5.9	6.1	5.7
236	CH(CH3)CN	50.9	50.9	56.5	47.9	47.9	53.5	36.5	36.5	39.7	.0	.0	2.1
237	CH(CH3)(4-CH3-C6H4)	40.7	40.9	52.5	33.2	33.3	44.9	19.2	19.1	31.2	-8.2	-8.1	-8.4
238	C(CH3)(NO2)SCH3	-	-	-	-	-	-	-	-	-	-	-	-
239	C(CH3)(NO2)SC6H5	-	-	-	-	-	-	-	-	-	-	-	-
240	C(CH3)(NO2)S /2,4-(NO2)2-C6H3/	-	-	-	-	-	-	-	-	-	-	-	-
241	CH(CH3)CH2CN	56.6	56.8	55.2	52.5	52.6	51.0	40.6	40.5	39.4	6.1	6.2	5.9
242	C(CH3)2NH2	-	-	-	-	-	-	37.6	37.4	34.8	-	-	7.9
243	C(CH3)2C6H5	35.6	35.6	40.1	27.4	27.4	32.0	24.7	22.5	29.3	.0	.0	.0
244	CIS-CH=CHCH3	43.5	46.8	49.3	40.1	43.5	46.0	35.4	38.4	41.3	.0	2.8	.0
245	TRANS-CH=CHCH3	50.6	50.8	49.7	47.6	47.7	46.7	42.6	42.6	41.9	5.5	5.7	5.4
246	CCL=CHCL	-	-	-	-	-	-	-	-	-	-	-	-
247	CCL=CCL2	44.8	44.8	60.6	44.2	44.2	60.0	-	-	-	.3	.3	-

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
248	3-BR-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
249	4-BR-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
250	4-I-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
251	2-OH-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
252	3-OH-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
253	2-NH2-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
254	3-NH2-C6H4	58.8	88.1	72.4	54.0	82.9	67.9	-	-	-	-18.3	13.8	-
255	4-NH2-C6H4	59.2	65.7	68.4	54.4	60.8	63.9	-	-	-	-10.1	.0	-
256	2-C6H5-C6H4	-	-	-	-	-	-	-	-	-	-	-	-
257	C6F5	-	-	-	-	-	-	-	-	-	-	-	-
258	GA(C2H5)2	12.8	11.6	12.4	4.9	3.4	6.6	-	-	-	.0	3.4	-
259	OC7H15	-24.7	-21.3	-27.4	-35.3	-31.6	-35.8	-	-	-	6.8	10.7	-
260	OCH(CH3)C5H11	-23.6	-20.2	-26.8	-34.1	-30.4	-35.1	-	-	-	7.7	11.6	-
261	1-PIPERIDYL	29.7	30.3	31.1	24.1	24.3	25.8	-	-	-	1.5	2.2	-
262	4-MORPHOLINYL	-	-	-	-	-	-	-	-	-	-	-	-
263	PERHYDRO-1,3,5--TRIAZIN-1-YL	-	-	-	-	-	-	-	-	-	-	-	-
264	C5H11	-	-	-	-	-	-	-	-	-	-	-	-
265	P(C2H5)2	15.8	16.9	13.6	7.6	8.0	5.2	-	-	-	7.0	8.0	-
266	SB(C2H5)2	-	-	-	-	-	-	-	-	-	-	-	-
267	CH2N(CH3)2	-	-	-	-	-	-	34.3	34.4	35.2	-	-	4.1
	s_o	.007	.007	.013	.006	.006	.019	.038	.040	.064	.072	.090	.132
	s^o	.35	.35	.63	.36	.34	.96	.62	.69	1.07	.38	.41	.55
	NE	262	263	342	270	261	407	181	185	227	255	267	172
	NR$_2$	120	116	122	119	116	132	89	88	105	119	117	86
	$\Delta S'_{const}$	-	-	9.80	-	-	9.80	-	-	9.80	-	-	-

Table 2

Experimental Data for Homolyzing Compounds R_iR_j Not Listed in Paper[4]

i and j correspond to the enumeration of R from Table 1

n - statistical factor

T_1 and T_2 are values of lower and upper limits of experimental temperatures in K

log A and E are activation parameters in sec^{-1}(A) and kcal/mole, respectively

ΔH^o_{f0} and ΔH^o_{f298} denote the heats of formation of reagents R_iR_j at 0 and 298.15 K in kcal/mole

I_{ij} is the interaction energy between R_i and R_j in compounds R_iR_j ($sec^{1,4-7}$), kcal/mole

In the column of notes an auxiliary two-symbol sign and indication to experimental methods of determination of kinetic parameters are reported. Following abbrevations are used: ST - investigation in static conditions, F - flow, T - toluene carrier technique, A - aniline carrier technique (variety of toluene carrier), SW- method of shock waves, WLR - wall-less reactor technique, VLPP - very low pressure pyrolysis, and LIT - analysis of literature experimental data

No.	i	j	n	T_1	T_2	log A	E	Source of log A and E	ΔH^o_{f0}	ΔH^o_{f298}	Source of ΔH^o_{f0}(ΔH^o_{f298})	I_{ij}	Notes
1	2	3	4	5	6	7	8	9	10	11	12	13	14
1/	90	190	3	953	1143	13.4	78	(10,P.391)	8.5	4.9	(9)	0.00	AB
2/	243	80	3	865	935	13.48	59.5	(10,P.402)	4.6	-5.4	(195)	9.57	AB
3/	237	80	2	865	935	13.3	60	(10,P.403)	16.4	6.9	(198)	10.87	AB
4/	220	190	3	1077	1098	13.3	78	(10,P.409)	-30.1	-34.5	(199)	0.00	AB
5/	134	80	1	980	1110	15.71	77.6	(10,P.417)	-16.6	-22	(200)	16.75	AB

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
6/	134	80	1	980	1110	15.71	77.6	(10,P.417)	-15.4	-20.8	(195)	-	BA
7/	100	132	1	900	900	16	68.2	(10,P.418)	-29.7	-36.4	(201)	14.62	AA
8/	134	160	2	1075	1150	16.2	87.5	(10,P.419)	19.2	12.3	(200)	-	AA
9/	18	1	1	363	403	15.39	32.3	(10,P.557)	4.3	2.5	(9)	-	AA
10/	18	1	1	363	383	14.96	31.75	(10,P.557)	4.3	2.5	(9)	-	AB
11/	80	3	1	977	1080	13.3	67.5	(10,P.493)	-5.3	-8.9	(202)	17.81	AB
12/	80	3	1	977	1080	13.3	67.5	(10,P.493)	-5	-8.6	(218)	-	BB
13/	201	83	2	605	677	15.5	47.1	(10,P.521)	22.1	12.4	(203)	-	AA
14/	201	83	2	605	677	15.5	47.1	(10,P.521)	16.4	6.7	(204)	-	BA
15/	69	84	2	502	714	16.2	40.4	(10,P.523)	20	10.4	(203)	-	AA
16/	69	84	2	513	573	16.4	40.7	(10,P.523)	20	10.4	(203)	-	AA
17/	69	84	2	502	714	16.2	40.4	(10,P.523)	19	9.4	(204)	-	BA
18/	69	84	2	513	573	16.4	40.7	(10,P.523)	19	9.4	(204)	-	BA
19/	203	160	2	896	960	16	68	(10,P.525)	101.2	93.8	(204)	-	AA
20/	203	160	2	896	960	16	68	(10,P.525)	97.1	90.7	(205)	-	BA
21/	62	80	4	932	990	15.4	78.8	(10,P.543)	-17.3	-26	(206)	-	AA
22/	62	80	4	932	990	15.4	78.8	(10,P.543)	-60.1	-68.8	(207,208)	-	BA
23/	17	2	1	373	403	12.36	27	(10,P.556)	4.3	3	(9)	-	AB
24/	80	190	4	1850	2500	15.1	104	(11)	-15.9	-17.8	(196)	0.00	AA SW
25/	80	190	4	1293	1388	16.35	107	(12)	-15.9	-17.8	(196)	0.00	AA SW
26/	100	190	3	920	970	15.96	88.9	(13)	17.5	12	(9)	0.00	AA ST
27/	100	190	3	1100	1800	16.9	90.8	(14)	17.5	12	(9)	0.00	AA SW
28/	139	190	2	1250	1600	17.1	81.3	(15)	13.9	7.1	(9)	0.00	AA SW
29/	160	190	6	1400	1900	15.2	102	(16)	24	19.8	(9)	0.00	AA SW
30/	14	190	3	2200	2600	12.82	98	(17)	-9.4	-11	(9)	0.00	AA SW
31/	14	190	3	2200	3300	15.74	107.8	(18)	-9.4	-11	(9)	0.00	AA SW
32/	80	80	1	1000	1500	16.9	89.5	(19)	-16.3	-20	(196)	15.52	AA SW
33/	80	80	1	813	833	16.6	88	(20)	-16.3	-20	(196)	15.52	AA ST
34/	80	80	1	840	913	16.72	88.85	(21)	-16.3	-20	(196)	15.52	AA ST
35/	80	80	1	1330	2500	16.31	87.9	(22)	-16.3	-20	(196)	15.52	AA SW
36/	80	80	1	1330	2500	16.85	90.1	(22)	-16.3	-20	(196)	15.52	AA SW

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
37/	80	80	1	750	1500	16.38	87.45	(23)	-16.3	-20	(196)	15.52	AA LIT
38/	80	80	1	840	840	16.37	88	(24)	-16.3	-20	(196)	15.52	AA ST
39/	80	80	1	840	913	16.8	89.1	(21)	-16.3	-20	(196)	15.52	AA ST
40/	80	80	1	1240	1500	15.45	84.24	(25)	-16.3	-20	(196)	15.52	AA SW
41/	80	80	1	1045	1172	15.6	84.9	(26)	-16.3	-20	(196)	15.52	AA SW
42/	80	80	1	1007	1241	15	82.1	(26)	-16.3	-20	(196)	15.52	AA SW
43/	80	80	1	1000	1105	15.7	83.7	(26)	-16.3	-20	(196)	15.52	AA SW
44/	80	80	1	1034	1126	16.5	88.1	(26)	-16.3	-20	(196)	15.52	AA SW
45/	80	80	1	1000	1241	17.2	91	(26)	-16.3	-20	(196)	15.52	AA SW
46/	80	80	1	841	913	16.52	87.9	(27)	-16.3	-20	(196)	15.52	AA ST
47/	80	80	1	823	913	16.63	88.4	(27)	-16.3	-20	(196)	15.52	AA ST
48/	82	80	2	783	833	17.3	83.7	(28)	-19.7	-25	(196)	12.41	AA ST
49/	82	80	2	973	1123	14.78	75	(29)	-19.7	-25	(196)	12.41	AA ST
50/	82	80	2	1100	1298	14.24	71.7	(30)	-19.7	-25	(196)	12.41	AA ST
51/	82	80	2	748	793	16.7	84.9	(31)	-19.7	-25	(196)	12.41	AA ST
52/	82	80	2	1048	1123	17.44	77.91	(32)	-19.7	-25	(196)	12.41	AA ST
53/	82	80	2	1215	1454	16.83	90.2	(33)	-19.7	-25	(196)	12.41	AA SW
54/	82	80	2	1215	1454	16.4	87.5	(33)	-19.7	-25	(196)	12.41	AA SW
55/	82	80	2	1050	1250	15.51	82.9	(33)	-19.7	-25	(196)	12.41	AA SW
56/	82	80	2	1300	1600	13.6	67.9	(34)	-19.7	-25	(196)	12.41	AA SW
57/	82	80	2	1400	2300	17.17	86.5	(35)	-19.7	-25	(196)	12.41	AA SW
58/	83	80	2	1290	1610	13.95	71.9	(36)	-23.6	-30	(196)	13.00	AA SW
59/	84	80	3	770	855	16.8	81.7	(37)	-25.2	-32.1	(196)	10.52	AA ST
60/	84	80	3	1090	1280	17.6	84.9	(38)	-25.2	-32.1	(196)	10.52	AA VLPP
61/	84	80	3	1090	1280	16.5	81.3	(38)	-25.2	-32.1	(196)	10.52	AA VLPP
62/	84	80	3	1090	1280	16.9	82.8	(38)	-25.2	-32.1	(196)	10.52	AA VLPP
63/	84	80	3	1090	1280	16.8	82.6	(38)	-25.2	-32.1	(196)	10.52	AA VLPP
64/	84	80	3	970	1031	15.92	85.42	(39)	-25.2	-32.1	(196)	10.52	AA WLR
65/	84	80	3	1300	1600	12.8	60.8	(34)	-25.2	-32.1	(196)	10.52	AB SW
66/	87	80	4	1050	1300	15.7	76	(40)	-31.8	-40.1	(197)	9.30	AA F
67/	87	80	4	1050	1300	16.52	80.6	(40)	-31.8	-40.1	(197)	9.30	AA SW

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
68/	87	80	4	703	743	17.6	84	(41)	-31.8	-40.1	(197)	9.30	AA F
69/	87	80	4	1000	1260	17.3	80.4	(42)	-31.8	-40.1	(197)	9.30	AA VLPP
70/	87	80	4	1070	1240	16.5	78	(43)	-31.8	-40.1	(197)	9.30	AA SW
71/	87	80	4	1140	1300	17.23	84	(44)	-31.8	-40.1	(197)	9.30	AA SW
72/	88	80	4	667	770	17	74.8	(45)	-32.7	-42.5	(9)	11.15	AA ST
73/	90	80	1	829	1040	15.5	72	(46)	5	0	(9)	12.73	AA F
74/	91	80	1	671	722	16.6	71	(47)	-2.3	-8.7	(9)	13.24	AA ST
75/	226	80	1	776	835	16.7	71.5	(48)	-	-		10.17	AA ST
76/	226	80	1	776	835	17.8	76	(48)	-	-		10.17	AA ST
77/	227	80	1	780	830	16.26	69.2	(49)	-	-		9.34	AA ST
78/	94	80	1	1052	1152	15.5	74.2	(50)	42.7	39.5	(9)	12.57	AA VLPP
79/	94	80	1	652	731	17.2	74.8	(51)	42.7	39.5	(9)	12.57	AA ST
80/	99	80	1	789	850	15.5	78.7	(52)	15.7	12.4	(209)	11.15	AA ST
81/	99	80	1	789	850	15.5	78.7	(52)	14.5	11.2	(210)	-	BA ST
82/	100	80	1	910	1089	14.7	70.1	(53)	13.9	7.1	(9)	13.04	AA T
83/	100	80	1	990	1190	15.85	74.4	(54)	13.9	7.1	(9)	13.04	AA VLPP
84/	100	80	1	1099	1227	15	71.9	(55)	13.9	7.1	(9)	13.04	AA VLPP
85/	100	80	1	1053	1234	15.3	72.7	(56)	13.9	7.1	(9)	13.04	AA VLPP
86/	100	80	1	770	820	14.4	70	(57)	13.9	7.1	(9)	13.04	AA ST
87/	100	80	1	873	998	15.7	74.49	(58)	13.9	7.1	(9)	13.04	AA ST
88/	100	80	1	876	1000	14.79	70.76	(58)	13.9	7.1	(9)	13.04	AA A
89/	100	80	1	873	1000	15.1	72	(58)	13.9	7.1	(9)	13.04	AA ST‡A
90/	101	80	1	1050	1200	15	70.7	(59)	8.1	0.3	(9)	13.04	AA VLPP
91/	102	80	1	1050	1200	15	71.6	(59)	7.6	-0.5	(9)	13.04	AA VLPP
92/	103	80	1	1050	1200	15	71.5	(59)	7.2	-0.8	(9)	13.04	AA VLPP
93/	221	80	1	1070	1200	15	70.2	(59)	1.3	-7.8	(211)	13.04	AA VLPP
94/	222	80	1	1050	1180	15	69	(59)	2.6	-6.5	(211)	13.04	AA VLPP
95/	223	80	1	1070	1200	15	71.2	(59)	0.7	-8.7	(211)	13.04	AA VLPP
96/	104	80	1	980	1150	15.6	71	(54)	31.2	23.1	(195)	13.00	AA VLPP
97/	104	80	1	980	1150	15.6	71.5	(54)	31.2	23.1	(195)	13.00	AA VLPP
98/	106	80	1	1125	1223	15	73.4	(55)	-	-		13.00	AA VLPP

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
99/	107	80	1	1099	1196	15	71.7	(55)	-	-		13.00	AA VLPP
100/	108	80	1	1125	1223	15	72.4	(55)	-	-		13.00	AA VLPP
101/	212	80	1	685	759	15.92	66.39	(60)	19.6	13.6	(60)	12.81	AA ST
102/	213	80	1	653	685	15.36	65	(61)	-	-		10.87	AA ST
103/	214	80	1	988	1234	16	72.6	(62)	35.5	30.8	(9)	13.63	AA VLPP
104/	233	80	1	768	813	16.95	81.5	(63)	-37.2	-39.7	(9)	16.75	AA ST
105/	233	80	1	768	813	16.59	79.7	(63)	-37.2	-39.7	(9)	16.75	AA ST
106/	233	80	1	751	793	16	81.7	(64)	-37.2	-39.7	(9)	16.75	AA ST
107/	233	80	1	800	1225	15.85	81.775	(65)	-37.2	-39.7	(9)	16.75	AA F
108/	233	80	1	770	1600	16.08	81.7	(66)	-37.2	-39.7	(9)	16.75	AA ST
109/	233	80	1	1350	1650	15.7	79.1	(66)	-37.2	-39.7	(9)	16.75	AA ST
110/	233	80	1	768	813	16.95	81.5	(63)	-38.7	-41.2	(9)	-	BA ST
111/	233	80	1	768	813	16.59	79.7	(63)	-38.7	-41.2	(9)	-	BA ST
112/	233	80	1	751	793	16	81.7	(64)	-38.7	-41.2	(9)	-	BA ST
113/	233	80	1	800	1225	15.85	81.775	(65)	-38.7	-41.2	(9)	-	BA F
114/	233	80	1	770	1600	16.08	81.7	(66)	-38.7	-41.2	(9)	-	BA ST
115/	233	80	1	1350	1650	15.7	79.1	(66)	-38.7	-41.2	(9)	-	BA ST
116/	132	80	2	1335	1650	16.43	81.7	(66)	-47.7	-51.7	(9)	16.75	AA ST
117/	235	80	1	1090	1250	16.2	82.3	(67)	12	7.5	(212)	13.32	AA VLPP
118/	235	80	1	1090	1250	16.2	82.3	(67)	12.6	8.1	(195)	-	BA VLPP
119/	139	80	2	971	1151	15.8	71.3	(56)	9.25	0.94	(9)	10.87	AA VLPP
120/	236	80	2	1074	1253	15.7	79	(68)	10.5	5.6	(212)	9.73	AA VLPP
121/	236	80	2	1074	1253	15.7	79	(68)	10.9	6.1	(195)	-	BA VLPP
122/	241	80	2	1011	1125	16.5	81.5	(67)	11.1	5	(195,213)	1.07	AA VLPP
123/	151	80	3	1023	1254	15.9	74.9	(69)	5.6	-0.8	(214)	8.79	AA VLPP
124/	215	80	3	930	1182	15.8	70.8	(70)	-	-		9.38	AA VLPP
125/	243	80	3	899	899	15.2	66.6	(71)	4.6	-5.4	(195)	9.57	AA ST
126/	243	80	3	929	1157	15.9	69.1	(56)	4.6	-5.4	(195)	9.57	AA VLPP
127/	244	80	2	1132	1298	16	80.1	(72)	3.5	-1.7	(9)	11.27	AA SW
128/	244	80	2	1132	1298	15.6	78.8	(72)	3.5	-1.7	(9)	11.27	AA SW
129/	245	80	2	1181	1323	16.6	86	(72)	2.2	-2.7	(9)	10.24	AA SW

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
130/	245	80	2	1181	1323	16.3	83.5	(72)	2.2	-2.7	(9)	10.24	AA SW
131/	82	82	1	1100	1270	16.8	82.5	(38)	-23.6	-30	(196)	9.92	AA VLPP
132/	82	82	1	1100	1270	15.6	78.6	(38)	-23.6	-30	(196)	9.92	AA VLPP
133/	82	82	1	1100	1270	16.4	80.9	(38)	-23.6	-30	(196)	9.92	AA VLPP
134/	82	82	1	1100	1270	16.5	82.4	(38)	-23.6	-30	(196)	9.92	AA VLPP
135/	82	82	1	693	803	15.5	79.1	(73)	-23.6	-30	(196)	9.92	AA LIT
136/	90	82	1	1006	1161	16	71.3	(74)	1.1	-5	(9)	10.17	AA SW
137/	99	82	1	1090	1250	15.4	76.7	(67)	12	7.5	(212)	8.88	AA VLPP
138/	99	82	1	1090	1250	15.4	76.7	(67)	12.6	8.1	(195)	-	BA VLPP
139/	100	82	1	989	1195	15.3	69.6	(75)	9.8	1.9	(9)	10.43	AA VLPP
140/	100	82	1	860	1021	15.6	71.5	(75)	9.8	1.9	(9)	10.43	AA A
141/	242	82	1	990	1181	16.5	76.5	(76)	-	-		6.99	AA SW
142/	90	83	1	977	1171	15.9	70.7	(77)	-2.5	-10	(9)	10.63	AA SW
143/	90	83	1	915	1153	15.9	70.8	(78)	-2.5	-10	(9)	10.63	AA VLPP
144/	94	83	1	985	1150	15.9	72.1	(79)	35.3	29.6	(9)	10.53	AA SW
145/	84	84	1	970	1250	17.9	80.2	(38)	-32.7	-42.5	(9)	7.13	AA VLPP
146/	84	84	1	970	1250	16.4	75.6	(38)	-32.7	-42.5	(9)	7.13	AA VLPP
147/	84	84	1	970	1250	16.4	74.6	(38)	-32.7	-42.5	(9)	7.13	AA VLPP
148/	84	84	1	970	1250	16.4	76.5	(38)	-32.7	-42.5	(9)	7.13	AA VLPP
149/	84	84	1	667	770	16.2	80.3	(45)	-32.7	-42.5	(9)	7.13	AA ST
150/	87	84	1	753	1197	16.46	72.9	(43)	-37.7	-49	(9)	7.70	AA ST
151/	99	84	1	1011	1123	15.4	73.1	(67)	11.1	5	(195,213)	7.50	AA VLPP
152/	100	84	1	922	1087	15.6	67.8	(75)	4.4	-5.2	(215)	8.84	AA VLPP
153/	94	211	1	1000	1172	16.1	72.9	(79)	-	-		10.88	AA SW
154/	214	211	1	1005	1209	16.2	73.1	(79)	-	-		11.80	AA SW
155/	91	86	1	970	1200	15.63	66	(80)	-	-		9.27	AA SW
156/	91	86	1	970	1200	15.9	67.4	(77)	-	-		9.27	AA SW
157/	94	86	1	990	1180	15.9	69.5	(79)	-	-		8.80	AA SW
158/	87	87	1	860	1140	16.8	69.3	(38)	-41.2	-54	(9)	9.70	AA VLPP
159/	87	87	1	860	1140	14	58.9	(38)	-41.2	-54	(9)	9.70	AA VLPP
160/	87	87	1	860	1140	16.4	68	(38)	-41.2	-54	(9)	9.70	AA VLPP

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
161/	87	87	1	860	1140	16.4	67.8	(38)	-41.2	-54	(9)	9.70	AA VLPP
162/	87	87	1	985	1141	16.44	68	(81)	-41.2	-54	(9)	9.70	AA SW
163/	87	87	1	985	1141	16.58	68.7	(81)	-41.2	-54	(9)	9.70	AA SW
164/	87	87	1	985	1141	16.43	68.5	(81)	-41.2	-54	(9)	9.70	AA SW
165/	87	87	1	985	1141	16.44	67.3	(81)	-41.2	-54	(9)	9.70	AA SW
166/	87	87	1	754	925	10.7	42.4	(82)	-41.2	-54	(9)	9.70	AA WLR
167/	87	87	1	713	815	17.08	70.6	(83)	-41.2	-54	(9)	9.70	AA ST
168/	87	87	1	713	1141	16.78	69.4	(83)	-41.2	-54	(9)	9.70	AA ST;SW
169/	87	87	1	758	917	16.5	70.9	(84)	-41.2	-54	(9)	9.70	AA F
170/	87	87	1	1000	1200	17.4	72.1	(84)	-41.2	-54	(9)	9.70	AA SW
171/	87	87	1	673	815	17.02	70.4	(85)	-41.2	-54	(9)	9.70	AA ST
172/	100	87	1	918	1064	15.5	64.3	(75)	-	-		7.81	AA VLPP
173/	90	90	1	300	950	16.3	58	(86)	25.7	20	(195)	10.51	AA VLPP
174/	90	90	1	300	950	15.65	56.6	(86)	25.7	20	(195)	10.51	AA VLPP
175/	100	94	1	850	1150	14.6	60.3	(87)	-	-		10.75	AA VLPP
176/	100	100	1	633	733	14.8	60.4	(88)	41.7	32.4	(216)	11.03	AA ST
177/	216	100	1	960	1245	14.7	63.9	(89)	-	-		9.23	AA VLPP
178/	114	182	1	1170	1410	16.9	92.3	(90)	-217.3	-220	(217)	-6.41	AA SW
179/	184	184	1	1310	1450	17.4	91.4	(91)	-	-		-0.04	AA SW
180/	114	184	1	1276	1442	16.6	93.5	(92)	-	-		-10.28	AA SW
181/	233	114	1	733	793	17	83	(93)	-	-		-1.87	AA ST
182/	233	114	1	744	792	16.63	80	(94)	-	-		-1.87	AA ST
183/	160	114	1	720	859	17.9	98.7	(95)	-137.2	-141.9	(219)	-7.91	AA ST
184/	115	115	1	611	676	17.75	68	(96)	-30.2	-32.1	(207)	13.88	AA ST
185/	115	115	1	611	676	17.75	68	(96)	-31.9	-33.8	(195)	-	BA ST
186/	115	115	1	611	676	17.75	68	(96)	-34.1	-36	(220)	-	BA ST
187/	132	132	1	648	690	16.5	67.7	(97)	-74.5	-78.4	(195,221)	21.88	AA ST
188/	132	132	1	822	905	15.8	66.8	(98)	-74.5	-78.4	(195,221)	21.88	AA F
189/	80	2	1	1680	2430	13.86	91.54	(99)	-18.7	-20.6	(195)	19.62	AA SW
190/	80	2	1	1680	2430	15.52	91.54	(99)	-18.7	-20.6	(195)	19.62	AA SW
191/	80	2	1	1680	2430	13.86	91.54	(99)	-17.4	-19.3	(9)	-	BA SW

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
192/	80	2	1	1680	2430	15.52	91.54	(99)	-17.4	-19.3	(9)	-	BA SW
193/	247	2	4	1450	1900	14.65	80	(100)	-3.3	-3.5	(195,222)	-	AA SW
194/	110	3	3	773	923	13.08	51	(101)	10.2	4	(194)	17.81	AA T
195/	110	3	3	773	923	13.08	51	(101)	16.2	10	(194)	-	BA T
196/	217	3	1	1040	1290	16	62.5	(102)	-37.8	-43	(102)	16.29	AA VLPP
197/	160	3	1	1030	1530	13.5	71.5	(16)	21.6	15.9	(194)	16.33	AA SW&T
198/	160	3	1	1000	1600	13.6	71.5	(103)	21.6	15.9	(194)	16.33	AA SW&T
199/	160	3	1	1018	1126	14.63	75.8	(104)	21.6	15.9	(194)	16.33	AA T
200/	160	3	1	1030	1530	13.5	71.5	(16)	27.3	21.6	(223)	-	BA ST
201/	160	3	1	1000	1600	13.6	71.5	(103)	27.3	21.6	(223)	-	BA ST
202/	160	3	1	1018	1126	14.63	75.8	(104)	27.3	21.6	(223)	-	BA ST
203/	160	3	1	1030	1530	13.5	71.5	(16)	32.9	27.2	(205)	-	BA ST
204/	160	3	1	1000	1600	13.6	71.5	(103)	32.9	27.2	(205)	-	BA ST
205/	160	3	1	1018	1126	14.63	75.8	(104)	32.9	27.2	(205)	-	BA ST
206/	160	3	1	1030	1530	13.5	71.5	(16)	30.8	25.1	(195)	-	BA ST
207/	160	3	1	1000	1600	13.6	71.5	(103)	30.8	25.1	(195)	-	BA ST
208/	160	3	1	1018	1126	14.63	75.8	(104)	30.8	25.1	(195)	-	BA ST
209/	160	3	1	1030	1530	13.5	71.5	(16)	30.4	24.7	(224)	-	BA ST
210/	160	3	1	1000	1600	13.6	71.5	(103)	30.4	24.7	(224)	-	BA ST
211/	160	3	1	1018	1126	14.63	75.8	(104)	30.4	24.7	(224)	-	BA ST
212/	83	4	1	853	1152	16.5	55.7	(105)	-3.4	-8.5	(225)	13.27	AA VLPP
213/	83	4	1	856	1235	15.5	54.9	(106)	-3.4	-8.5	(225)	13.27	AA VLPP
214/	83	4	1	853	1152	16.5	55.7	(105)	-2.2	-7.3	(195)	-	BA VLPP
215/	83	4	1	856	1235	15.5	54.9	(106)	-2.2	-7.3	(195)	-	BA VLPP
216/	114	4	1	623	723	15.89	48.8	(107)	-142.6	-144	(194)	-0.66	AA ST
217/	114	4	1	623	723	16.72	52.8	(108)	-142.6	-144	(194)	-0.66	AA ST
218/	114	4	1	623	723	15.89	48.8	(107)	-138	-139.4	(226)	-	BA ST
219/	114	4	1	623	723	16.72	52.8	(108)	-138	-139.4	(226)	-	BA ST
220/	14	14	1	999	999	13.9	55	(109)	26.2	22.8	(195)	-	AA SW
221/	14	14	1	1100	1400	13.6	53	(110)	26.2	22.8	(195)	-	AA SW
222/	41	14	1	865	1076	17.6	63	(111)	26.2	19.9	(9,227)	-	AA VLPP

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
223/	80	14	1	1275	2400	10.84	48.15	(112)	-2	-5.5	(195)	23.17	AA SW
224/	89	14	1	990	1181	15.9	78.9	(76)	-	-		14.23	AA SW
225/	80	40	1	952	1257	15.1	66.7	(113)	28.2	21.6	(228)	17.81	AA VLPP
226/	80	40	1	952	1257	15.1	66.7	(113)	27	20.4	(195)	-	BA VLPP
227/	80	43	2	927	1219	15.1	64.7	(113)	30.9	22.8	(228)	11.70	AA VLPP
228/	80	43	2	927	1219	15.1	64.7	(113)	28.2	20.1	(195)	-	BA VLPP
229/	160	16	1	763	953	15.4	49	(114)	55.8	51.5	(229)	-	AA VLPP
230/	80	17	1	673	773	14.82	57	(115)	-14.55	-17.9	(9)	24.03	AA ST
231/	130	17	4	360	715	17.1	40	(116)	24.4	18.5	(230)	44.87	AA SW;LIT
232/	160	17	1	728	803	15.7	67.3	(117)	20.7	15.7	(231)	22.85	AA ST
233/	160	17	1	728	803	15.7	67.3	(117)	20	15	(230)	-	BA ST
234/	254	17	1	703	773	17.5	72	(118)	24.5	18.6	(232,233)	-	AA ST
235/	254	17	1	573	623	10.55	43	(119)	24.5	18.6	(232,233)	-	AA ST
236/	255	17	1	603	643	12.36	47.9	(119)	20.1	14.2	(234,233)	-	AA ST
237/	255	17	1	713	783	17.5	79.7	(118)	20.1	14.2	(234,233)	-	AA ST
238/	164	17	2	623	723	12.3	48.9	(120)	26.3	20.3	(230)	-	AA ST
239/	165	17	2	693	753	16.9	68	(118)	19.2	12.9	(230)	-	AA ST
240/	165	17	2	693	753	16.9	68	(118)	21.4	15.1	(230)	-	BA ST
241/	166	17	2	693	743	17.1	68.6	(118)	18.3	12	(230)	-	AA ST
242/	172	17	3	653	743	17.2	67.3	(118)	34	27.4	(230)	-	AA ST
243/	172	17	3	653	743	17.2	67.3	(118)	25.9	19.3	(230)	-	BA ST
244/	169	17	1	653	723	16.6	65.9	(121)	13.7	7.4	(235)	-	AA ST
245/	177	17	1	593	613	12.4	46.9	(120)	13.4	5.8	(235)	-	AA ST
246/	80	45	2	580	657	15.19	49.9	(122)	40.3	35.5	(236)	-	AA T
247/	80	45	2	534	657	13.9	46.3	(122)	40.3	35.5	(236)	-	AA ST;LIT
248/	84	50	2	528	528	18.1	51.8	(123)	19.3	8.6	(237)	-	AA ST
249/	84	50	2	650	850	16.6	47.9	(124)	19.3	8.6	(237)	-	AA VLPP
250/	84	50	2	494	540	15.4	44.6	(125)	19.3	8.6	(237)	-	AA ST
251/	84	50	2	518	573	17.33	50.5	(126)	19.3	8.6	(237)	-	AA ST
252/	84	50	2	503	544	16.31	47.6	(126)	19.3	8.6	(237)	-	AA ST
253/	84	50	2	494	546	14.6	42.5	(127)	19.3	8.6	(237)	-	AA ST

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
254/	84	50	2	523	573	16.2	47	(128)	19.3	8.6	(237)	-	AA ST
255/	84	50	2	528	528	18.1	51.8	(123)	30.2	19.5	(238)	-	BA ST
256/	84	50	2	650	850	16.6	47.9	(124)	30.2	19.5	(238)	-	BA ST
257/	84	50	2	494	540	15.4	44.6	(125)	30.2	19.5	(238)	-	BA ST
258/	84	50	2	518	573	17.33	50.5	(126)	30.2	19.5	(238)	-	BA ST
259/	84	50	2	503	544	16.31	47.6	(126)	30.2	19.5	(238)	-	BA ST
260/	84	50	2	494	546	14.6	42.5	(127)	30.2	19.5	(238)	-	BA ST
261/	84	50	2	523	573	16.2	47	(128)	30.2	19.5	(238)	-	BA ST
262/	87	53	2	471	531	15.94	41.9	(126)	2.9	-10.4	(237)	-	AA ST
263/	87	53	2	550	725	16.4	42.8	(124)	2.9	-10.4	(237)	-	AA VLPP
264/	87	53	2	471	531	15.94	41.9	(126)	4.6	-8.7	(236)	-	BA ST
265/	87	53	2	550	725	16.4	42.8	(124)	4.6	-8.7	(236)	-	BA VLPP
266/	24	16	1	440	473	15.8	41.2	(129)	-13.7	-16.8	(194)	-	AA ST
267/	24	16	1	440	473	15.8	41.2	(129)	-12.9	-16	(129)	-	BA ST
268/	24	16	1	440	473	15.8	41.2	(129)	-12.5	-15.6	(194)	-	BA ST
269/	24	16	1	440	473	15.8	41.2	(129)	-12.2	-15.3	(195)	-	BA ST
270/	24	16	1	440	473	15.8	41.2	(129)	-11.8	-14.9	(194)	-	BA ST
271/	26	16	1	435	470	16	41.8	(130)	-20	-24.2	(200)	-	AA ST
272/	26	16	1	435	470	16	41.8	(130)	-20.6	-24.8	(195)	-	BA ST
273/	27	16	1	566	800	14.7	37.7	(131)	-24.6	-30.1	(200)	-	AA VLPP
274/	27	16	1	566	800	16.5	40	(131)	-24.6	-30.1	(200)	-	AA VLPP
275/	28	16	1	499	499	16.2	41	(132)	-26.2	-31.9	(239)	-	AA ST
276/	29	16	1	590	750	16.5	41	(133)	-27.9	-34.8	(239)	-	AA VLPP
277/	192	16	1	403	433	16.2	40.9	(134)	-29.5	-36.5	(239)	-	AA ST
278/	30	16	1	650	770	15.8	39.3	(131)	-33.7	-41	(239)	-	AA VLPP
279/	30	16	1	650	770	16.3	40.3	(131)	-33.7	-41	(239)	-	AA VLPP
280/	30	16	1	393	433	16.3	40.3	(135)	-33.7	-41	(239)	-	AA ST
281/	30	16	1	650	850	16.4	42.8	(136)	-33.7	-41	(239)	-	AA ST
282/	31	16	1	393	423	16.3	40.3	(137)	-37.2	-45.8	(137)	-	AA ST
283/	6	17	1	900	1200	15.3	49	(138)	-29.8	-32.2	(194)	-	AA SW
284/	6	17	1	295	1200	15.1	47.7	(138)	-29.8	-32.2	(194)	-	AA SW

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
285/	24	17	1	700	1200	16.3	41	(139)	-25.1	-28.7	(195,240)	-	AA SW
286/	26	17	1	700	1200	16.3	41	(139)	-31.9	-36.8	(195)	-	AA SW
287/	28	17	1	700	1200	16.3	41	(139)	-39.3	-45.7	(195)	-	AA SW
288/	18	17	2	300	500	14.93	22	(140)	5.7	2.7	(9)	-	AA LIT
289/	18	17	2	200	300	14.98	22	(140)	5.7	2.7	(9)	-	AA LIT
290/	41	17	1	453	513	13.7	38.9	(141)	4.6	-1.2	(241)	-	AA ST
291/	41	17	1	453	513	13.7	38.9	(141)	5.5	-0.3	(195)	-	BA ST
292/	261	17	1	473	513	14.8	42.1	(141)	-3.9	-10.6	(241)	-	AA ST
293/	259	6	1	523	633	15.85	41.5	(142)	-54.4	-66	(242)	-	AA F
294/	260	6	1	523	633	16.04	43.5	(142)	-55.3	-66.8	(242)	-	AA F
295/	24	24	1	383	413	15.5	37	(143)	-25.5	-30	(195)	-	AA ST
296/	24	24	1	391	432	15.7	37.1	(144)	-25.5	-30	(195)	-	AA ST
297/	24	24	1	383	413	15.5	37	(143)	-27.5	-32	(243)	-	BA ST
298/	24	24	1	391	432	15.7	37.1	(144)	-27.5	-32	(243)	-	BA ST
299/	30	30	1	403	440	15.56	37.44	(145)	-67.3	-81.6	(244,195)	-	AA ST
300/	30	30	1	504	527	16.48	39.04	(146)	-67.3	-81.6	(244,195)	-	AA ST
301/	30	30	1	413	438	15.82	37.77	(147)	-67.3	-81.6	(244,195)	-	AA ST
302/	30	30	1	373	433	15.62	37.51	(148)	-67.3	-81.6	(244,195)	-	AA ST
303/	30	30	1	373	433	15.94	38.18	(148)	-67.3	-81.6	(244,195)	-	AA ST
304/	30	30	1	363	397	15.99	38.31	(148)	-67.3	-81.6	(244,195)	-	AA ST
305/	30	30	1	391	413	15.14	36.37	(148)	-67.3	-81.6	(244,195)	-	AA ST
306/	30	30	1	506	660	15.6	36.8	(149)	-67.3	-81.6	(244,195)	-	AA VLPP
307/	30	30	1	506	660	15.6	37.4	(149)	-67.3	-81.6	(244,195)	-	AA VLPP
308/	30	30	1	528	677	15.33	36.4	(150)	-67.3	-81.6	(244,195)	-	AA SW
309/	30	30	1	391	441	15.82	37.73	(151)	-67.3	-81.6	(244,195)	-	AA ST
310/	80	6	1	980	1120	15.4	80	(152)	-45.4	-47.9	(9)	25.89	AA ST
311/	80	6	1	1600	2000	15.97	89.9	(153)	-45.4	-47.9	(9)	25.89	AA SW
312/	80	24	2	1063	1223	15.33	76.6	(154)	-40.1	-44.3	(194)	25.89	AA F
313/	80	24	2	680	850	16.5	83	(155)	-40.1	-44.3	(194)	25.89	AA ST
314/	80	24	2	790	850	16.6	83.7	(155)	-40.1	-44.3	(194)	25.89	AA ST
315/	80	24	2	680	740	16.5	82	(155)	-40.1	-44.3	(194)	25.89	AA ST

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
316/	80	24	2	680	1200	16	80.5	(155)	-40.1	-44.3	(194)	25.89	AA ST
317/	80	24	2	680	1200	16.3	81.4	(155)	-40.1	-44.3	(194)	25.89	AA ST
318/	80	193	1	1050	1260	15.8	66.3	(102)	-29	-34.1	(245)	-	AA VLPP
319/	82	26	2	783	823	14.3	77.5	(156)	-53.2	-59.8	(246)	20.70	AA ST
320/	82	26	2	763	796	15.4	76.8	(157)	-53.2	-59.8	(246)	20.70	AA ST
321/	82	26	2	763	823	15.7	81	(158)	-53.2	-59.8	(246)	20.70	AA ST
322/	82	26	2	783	823	14.3	77.5	(156)	-53.7	-60.3	(195)	-	BA ST
323/	82	26	2	763	796	15.4	76.8	(157)	-53.7	-60.3	(195)	-	BA ST
324/	82	26	2	763	823	15.7	81	(158)	-53.7	-60.3	(195)	-	BA ST
325/	100	24	1	1000	1000	14.5	65.2	(159)	-	-		22.28	AA VLPP
326/	82	38	1	950	1220	15.3	60.4	(159)	-18.5	-25.4	(244)	23.44	AA VLPP
327/	82	38	1	950	1220	15.3	60.4	(159)	-19.4	-26.3	(159)	-	BA VLPP
328/	90	38	1	720	983	14.6	48.5	(159)	-	-		24.75	AA VLPP
329/	25	1	1	496	506	14.33	43.3	(160)	-181.3	-183.4	(247)	-	AA ST
330/	25	1	1	473	554	14.9	45	(161)	-181.3	-183.4	(247)	-	AA ST
331/	25	1	1	496	506	14.33	43.3	(160)	-181.7	-183.8	(217)	-	BA ST
332/	25	1	1	473	554	14.9	45	(161)	-181.7	-183.8	(217)	-	BA ST
333/	87	21	1	699	699	17.34	57.9	(162)	-34.6	-41.6	(248)	9.94	AA ST
334/	100	59	1	837	1138	14.7	56	(163)	10.6	3.8	(249)	14.41	AA VLPP
335/	87	199	2	633	686	15.1	54.7	(164)	-52	-64.8	(250)	9.94	AA ST
336/	87	199	2	633	686	16.3	59.3	(164)	-52	-64.8	(250)	9.94	AA ST
337/	87	199	2	633	739	16.7	59.3	(164)	-52	-64.8	(250)	9.94	AA F
338/	87	199	2	633	686	15.1	54.7	(164)	-47.5	-60.3	(251)	-	BA ST
339/	87	199	2	633	686	16.3	59.3	(164)	-47.5	-60.3	(251)	-	BA ST
340/	87	199	2	633	739	16.7	59.8	(164)	-47.5	-60.3	(251)	-	BA F
341/	80	60	1	946	1250	15.3	63.6	(163)	14	8.3	(249)	-	AA VLPP
342/	80	63	2	822	1015	13.3	54	(165)	17.2	13.1	(204)	-	AB T
343/	82	200	2	669	762	14.3	49	(166)	19.5	13	(204)	-	AB T
344/	82	200	2	669	762	14.3	49	(166)	16.7	10.2	(204)	-	BB T
345/	82	258	3	567	651	15.7	46.5	(167)	-3.4	-14.4	(252)	-	AB T
346/	82	258	3	567	651	15.7	46.5	(167)	-7	-18	(253)	-	BB T

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
347/	80	62	4	989	1149	14.1	72	(168)	-17.3	-26	(206)	-	AA WLR
348/	80	62	4	955	1055	17.6	84.9	(169)	-17.3	-26	(206)	-	AA F
349/	80	62	4	810	980	14.3	67.6	(170)	-17.3	-26	(206)	-	AA ST
350/	80	62	4	989	1149	14.1	72	(168)	-60.1	-68.8	(207,208)	-	BA WLR
351/	80	62	4	955	1055	17.6	84.9	(169)	-60.1	-68.8	(207,208)	-	BA F
352/	80	62	4	810	980	14.3	67.6	(170)	-60.1	-68.8	(207,208)	-	BA ST
353/	80	206	4	1078	1242	17	77	(171)	-12.5	-20.7	(254)	-	AA SW
354/	80	206	4	798	818	15.37	68.9	(172)	-12.5	-20.7	(254)	-	AA ST
355/	80	206	4	1050	1050	17.5	81	(173)	-12.5	-20.7	(254)	-	AA VLPP
356/	80	206	4	1175	1175	16.5	80.5	(173)	-12.5	-20.7	(254)	-	AA VLPP
357/	80	206	4	1300	1300	16.2	80	(173)	-12.5	-20.7	(254)	-	AA VLPP
358/	80	206	4	1175	1300	16	78	(173)	-12.5	-20.7	(254)	-	AA VLPP
359/	80	75	4	747	884	13.9	55.4	(168)	3.4	-4.1	(255)	-	AA WLR
360/	80	75	4	747	884	13.9	55.4	(168)	2.9	-4.6	(204)	-	BA WLR
361/	80	75	4	747	884	13.9	55.4	(168)	-3.5	-11	(256)	-	BA WLR
362/	80	75	4	747	884	13.9	55.4	(168)	-6.1	-13.6	(257)	-	BA WLR
363/	82	209	4	725	833	16	59.3	(174)	6.9	-8.1	(255)	-	AA T
364/	82	209	4	725	833	16	59.3	(174)	4.3	-10.7	(204)	-	BA T
365/	82	209	4	725	833	16	59.3	(174)	3	-12	(258)	-	BA T
366/	82	209	4	725	833	16	59.3	(174)	-1.7	-16.7	(256)	-	BA T
367/	80	76	4	890	1060	13.25	41.2	(175)	40.1	32.6	(204)	-	AA SW
368/	80	76	4	890	1060	13.25	41.2	(175)	30.7	23.2	(257)	-	BA SW
369/	82	77	4	650	800	16.3	49	(173)	38.8	25.8	(204)	-	AA VLPP
370/	82	77	4	650	800	18	53.6	(173)	38.8	25.8	(204)	-	AA VLPP
371/	82	77	4	725	725	18	53.3	(173)	38.8	25.8	(204)	-	AA VLPP
372/	82	77	4	800	800	18	53.1	(173)	38.8	25.8	(204)	-	AA VLPP
373/	191	1	6	1100	1450	16.52	70.3	(176)	-510.8	-509.4	(9)	-	AA SW
374/	265	82	3	850	1050	16	63	(173)	-21.6	-32.8	(259)	-	AA VLPP
375/	265	82	3	850	1050	17.5	67	(173)	-21.6	-32.8	(259)	-	AA VLPP
376/	265	82	3	850	1050	17.1	66.7	(173)	-21.6	-32.8	(259)	-	AA VLPP
377/	265	82	3	1050	1050	16.7	66.4	(173)	-21.6	-32.8	(259)	-	AA VLPP

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
378/	160	190	6	1900	2400	17.3	118.0	(260)	24	19.8	(9)	0.00	AA SW
379/	100	80	1	950	1100	15.3	72.7	(261)	13.9	7.1	(9)	13.04	AA VLPP
380/	100	216	1	950	1100	14.7	60.9	(261)	-	-		9.23	AA VLPP
381/	100	267	1	950	1100	14.8	58.7	(261)	-	-		9.28	AA VLPP
382/	216	216	1	920	1050	15.5	65.1	(262)	1.9	-4.1	(265)	7.73	AA VLPP
383/	267	267	1	1050	1180	15.6	63.2	(262)	-	-		8.20	AA VLPP
384/	157	157	1	1600	1900	16.61	93.4	(263)	29.8	26.3	(9)	13.16	AA SW
385/	48	82	2	508	598	16	49.6	(264)	-	-		-	AA ST
386/	210	81	2	1215	1454	16.83	90.2	(33)	-	-		-	AA SW
387/	225	80	1	900	1100	15.6	66.3	(54)	-	-		-	AA VLPP
388/	225	80	1	900	1100	15.6	67	(54)	-	-		-	AA VLPP
389/	224	3	1	1000	1073	14.54	53.8	(177)	-	-		-	AB T
390/	257	4	1	900	978	15.9	69.2	(178)	-	-		-	AB T
391/	257	4	1	900	972	15.4	67	(178)	-	-		-	AB T
392/	41	41	1	720	930	17.7	54	(111)	-	-		-	AA VLPP
393/	114	16	1	740	950	15.6	41.5	(179)	-	-		-	AA SW
394/	257	16	1	698	943	15.3	48	(114)	-	-		-	AA VLPP
395/	230	17	3	599	599	16.2	30.8	(180)	-	-		-	AA ST
396/	231	17	3	599	599	16	31.5	(180)	-	-		-	AA ST
397/	232	17	3	599	599	16.2	31.2	(180)	-	-		-	AA ST
398/	238	17	3	599	599	18	38.2	(180)	-	-		-	AA ST
399/	239	17	3	599	599	17.75	38.5	(180)	-	-		-	AA ST
400/	240	17	3	599	599	17.55	37.5	(180)	-	-		-	AA ST
401/	161	17	1	673	743	17	67.3	(118)	-	-		-	AA ST
402/	162	17	1	693	743	17.4	70.2	(118)	-	-		-	AA ST
403/	163	17	1	693	763	17.4	71.7	(118)	-	-		-	AA ST
404/	248	17	1	703	773	17.4	71	(118)	-	-		-	AA ST
405/	249	17	1	703	773	17.5	72.3	(118)	-	-		-	AA ST
406/	250	17	1	713	773	17.5	71.6	(118)	-	-		-	AA ST
407/	251	17	1	663	733	12.6	52.4	(120)	-	-		-	AB ST
408/	252	17	1	703	773	17.4	71.2	(118)	-	-		-	AA ST

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
409/	253	17	1	603	653	16.9	63.4	(119)	-	-		-	AA ST
410/	253	17	1	673	743	13.5	57.5	(120)	-	-		-	AB ST
411/	168	17	1	673	743	16.9	68	(121)	-	-		-	AA ST
412/	256	17	1	663	733	16	62.9	(118)	-	-		-	AA ST
413/	176	17	1	673	743	12.6	49.4	(120)	-	-		-	AB ST
414/	82	48	2	518	581	15.1	47.2	(181)	-	-		-	AB ST
415/	82	48	2	700	950	16.4	49.7	(124)	-	-		-	AA VLPP
416/	82	48	2	700	950	15.4	47.8	(124)	-	-		-	AA VLPP
417/	82	48	2	546	675	14.2	44.5	(182)	-	-		-	AB T
418/	82	48	2	530	598	15.8	49	(183)	-	-		-	AB ST
419/	82	48	2	553	623	15.8	49	(128)	-	-		-	AB ST
420/	82	50	1	533	593	16.5	49.2	(182)	-	-		-	AB T
421/	196	211	2	483	533	15.6	40.6	(182)	-	-		-	AB T
422/	114	47	2	720	1050	16.2	55.2	(184)	-	-		-	AA VLPP
423/	160	198	2	653	713	12.61	53.4	(185)	-	-		-	AB F
424/	160	198	2	642	711	16.6	66.4	(186)	-	-		-	AA ST
425/	197	82	1	654	689	15.72	51	(187)	-	-		-	AB F
426/	195	16	1	392	445	14.26	33.8	(188)	-	-		-	AB ST
427/	42	17	1	453	513	15.1	41.6	(141)	-	-		-	AB ST
428/	262	17	1	483	518	13.6	38.9	(141)	-	-		-	AB ST
429/	263	17	1	499	499	15.58	40.4	(189)	-	-		-	AB ST
430/	31	31	1	523	633	15.8	36.4	(149)	-	-		-	AA VLPP
431/	25	25	1	480	580	15.2	46.2	(161)	-	-		-	AB ST
432/	194	194	1	381	422	16.2	35.5	(190)	-	-		-	AA ST
433/	100	32	1	650	900	16.63	53.74	(191)	-	-		-	AA VLPP
434/	207	80	3	764	858	15.82	62.8	(192)	-	-		-	AB T
435/	78	80	3	690	803	15.3	55.9	(193)	-	-		-	AB T
436/	266	82	3	725	850	16.2	52	(173)	-	-		-	AA VLPP
437/	266	82	3	725	725	18	53.6	(173)	-	-		-	AA VLPP
438/	266	82	3	775	775	17.8	56.2	(173)	-	-		-	AA VLPP
439/	266	82	3	850	850	17.6	55.9	(173)	-	-		-	AA VLPP

Table 3

Results of the Data Treatment According to Eq. (7)

NE - number of lines

r - correlation coefficient

s - standard deviation

Significantly deviating lines were excluded according to the Student's criterion on the confidence level 0.99

Set of initial data	T_1	T_2	T_1/T_2	$\varkappa$	a	NE	r	s	log A_o
The total set	766.6	907.8	0.84444	0.844 ± 0.002	2.354 ± 0.010	696	0.9985	0.23	15.10 ± 0.06
				0.845 ± 0.002	2.364 ± 0.009	686	0.9987	0.21	15.22 ± 0.06
	700	800	0.875	0.847 ± 0.001	1.888 ± 0.008	696	0.9993	0.18	14.98 ± 0.07
				0.874 ± 0.001	1.897 ± 0.008	686	0.9993	0.17	15.11 ± 0.06
The data of the high-pressure limit	786.5	944.2	0.83298	0.834 ± 0.002	2.615 ± 0.010	498	0.9989	0.20	15.74 ± 0.06
				0.833 ± 0.001	2.637 ± 0.008	479	0.9993	0.16	15.82 ± 0.05
				0.830 ± 0.001	2.650 ± 0.005	360	0.9998	0.10	15.57 ± 0.03
	700	800	0.875	0.875 ± 0.001	1.956 ± 0.008	498	0.9996	0.15	15.64 ± 0.06
				0.875 ± 0.001	1.971 ± 0.007	479	0.9997	0.12	15.72 ± 0.05

* The number of lines after exclusion of markedly deviating lines according to Student on the confidence limit 0.95.

Table 4

Results of the Statistical Treatment in the Coordinates of Eqs. (10) - (14)

NRD - the number of different radicals with unknown $\Delta H^{\neq}_{R\bullet}$, $\Delta\Delta H^{\neq}_{R\bullet}$ or $\Delta S^{\neq}_{R\bullet}$ during MLRA; NRT - the total number of different radicals whose $\Delta H^{\neq}_{R\bullet}$ ($\Delta\Delta H^{\neq}_{R\bullet}$, $\Delta S^{\neq}_{R\bullet}$) values are determined.

The symbols s_o, s, NE, and NRN are the same as in Table 1.

Numbers of order for variants 1 - 9 correspond to those reported in Table 1. Variant 10 is identical with version 1 but only the lines more strictly belonging to the high-pressure region are included.

Variant	Approximation	NE	NRN	s_o	s, kcal/mol
1	2	3	4	5	6
1) NRD=86 NRT=143	INITIAL	595	162	0.121	5.65
	SET	552	159	0.664	3.89
	0	552	159	0.071	3.40
		502	149	0.397	2.10
	1	463	141	0.029	1.38
		412	135	0.216	1.13
	2	371	129	0.015	0.73
		342	128	0.136	0.70
	3	301	121	0.009	0.44
		276	120	0.086	0.45
	4	262	120	0.007	0.35
		255	119	0.072	0.38
2) NRD=86 NRT=143	INITIAL	458	162	0.873	5.83
	SET	583	160	0.092	4.33
	0	446	160	0.773	4.79
		536	152	0.045	2.08
	1	465	143	0.315	1.51
		440	139	0.025	1.16
	2	386	130	0.192	0.93
		350	126	0.013	0.62
	3	319	124	0.126	0.60
		287	117	0.008	0.40
	4	267	117	0.086	0.41
		263	116	0.007	0.35

Table 4 continued

1	2	3	4	5	6
3)	INITIAL SET	595	162	0.108	5.02
NRD=86 NRT=143		342	122	0.013	0.63
4)	INITIAL	595	162	0.121	5.67
NRD=86 NRT=143	SET	550	158	0.670	3.92
	0	550	158	0.071	3.39
		501	148	0.400	2.11
	1	426	133	0.022	1.05
		401	131	0.203	1.05
	2	372	129	0.015	0.74
		352	128	0.149	0.77
	3	327	124	0.010	0.54
		305	124	0.103	0.53
	4	270	119	0.006	0.36
		254	118	0.071	0.38
5)	INITIAL	458	162	0.873	5.83
NRD=86 NRT=143	SET	583	160	0.093	4.35
	0	446	160	0.773	4.79
		532	151	0.044	2.04
	1	445	138	0.282	1.34
		406	130	0.018	0.90
	2	381	128	0.186	0.90
		350	126	0.012	0.62
	3	323	125	0.126	0.61
		309	123	0.009	0.47
	4	279	119	0.090	0.44
		261	116	0.006	0.34
6)	INITIAL SET	595	162	0.106	4.97
NRD=86 NRT=143		407	132	0.019	0.96
7)	INITIAL	308	126	0.243	5.00
NRD=53 NRT=117	SET	299	123	0.665	3.49
	0	299	123	0.184	3.83
		275	115	0.423	1.95
	1	267	112	0.093	1.82
		251	107	0.324	1.43
	2	219	97	0.057	0.95
		208	94	0.199	0.82
	3	199	94	0.047	0.77
		189	90	0.163	0.67
	4	181	89	0.038	0.62
		172	86	0.132	0.55

Table 4 continued

1	2	3	4	5	6
8)	INITIAL	308	126	0.816	5.11
NRD=53 NRT=117	SET	288	119	0.157	3.13
	0	288	119	0.624	3.55
		273	113	0.104	2.07
	1	243	107	0.304	1.37
		228	102	0.065	1.16
	2	206	93	0.196	0.84
		199	92	0.046	0.81
	3	195	90	0.173	0.75
		193	90	0.042	0.75
	4	191	88	0.169	0.72
		185	88	0.040	0.69
9)	INITIAL SET	308	126	0.252	4.56
NRD=53 NRT=117		227	105	0.064	1.07
10)	INITIAL	442	118	0.114	5.68
NRD=69 NRT=121	SET	395	113	0.608	3.14
		395	113	0.050	2.60
		368	107	0.386	1.91
		327	102	0.022	1.11
		296	98	0.195	0.95
		265	92	0.012	0.61
		249	90	0.128	0.62
		215	88	0.006	0.36
		203	88	0.072	0.37
		181	84	0.004	0.23
		165	82	0.042	0.23

Table 5

List of Reactions (Combinations of Numbers of Order for Radicals R_i and R_j) According to Table 1 and Corresponding Numbers of Included Lines at Different Approximations of Iterative Procedure for Variant 1 in Table 1.

No.	i	j	Approximation											
			Initial set		0		1		2		3		4	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1/	80	190	7	7	7	7	3	3	1	1	1	1	1	1
2/	91	190	1	1	1	1	1	1	1	1	0	0	0	0
3/	100	190	5	5	5	4	4	2	0	0	0	0	0	0
4/	101	190	1	1	1	1	0	0	0	0	0	0	0	0
5/	102	190	1	1	1	1	1	1	0	0	0	0	0	0
6/	103	190	3	3	3	3	3	3	3	3	2	2	2	2
7/	80	80	26	26	26	26	23	23	19	19	16	16	13	13
8/	84	80	9	8	8	6	5	5	4	4	4	4	3	3
9/	87	80	14	14	14	14	14	14	11	10	2	2	2	2
10/	157	80	1	1	1	1	1	1	1	1	1	1	1	1
11/	90	80	4	4	4	3	3	2	1	1	1	1	1	1
12/	88	80	2	2	2	2	1	1	1	1	1	1	1	1
13/	100	80	13	13	13	13	13	13	13	13	11	11	10	10
14/	139	80	2	2	2	2	2	2	2	2	1	1	1	1
15/	169	80	3	1	1	1	1	1	1	1	1	1	1	1
16/	24	80	8	8	8	7	7	7	7	7	7	6	4	4
17/	132	80	5	4	4	3	3	3	3	3	1	1	1	1
18/	17	80	7	7	7	6	6	4	3	3	3	2	2	2
19/	21	80	1	1	1	1	1	1	1	1	0	0	0	0
20/	61	80	1	1	1	1	1	0	0	0	0	0	0	0
21/	4	80	2	2	2	1	0	0	0	0	0	0	0	0
22/	82	82	6	6	6	6	6	6	4	4	4	4	3	3
23/	89	82	1	1	1	1	1	1	1	1	1	1	1	1
24/	100	82	4	3	3	3	3	3	3	3	3	3	2	2
25/	21	82	1	1	1	1	1	1	1	1	1	1	1	1
26/	84	84	6	6	6	5	5	4	3	3	2	2	2	2
27/	87	84	2	2	2	2	2	2	2	2	1	1	1	1
28/	89	84	1	1	1	1	1	1	1	1	1	1	1	1
29/	87	87	15	13	13	13	13	13	12	12	11	11	10	10
30/	110	3	4	4	4	3	2	2	2	1	1	1	1	1
31/	116	3	3	3	3	2	2	2	2	2	2	2	2	2
32/	114	3	2	2	2	0	0	0	0	0	0	0	0	0
33/	115	3	2	2	2	2	2	1	0	0	0	0	0	0
34/	160	3	16	14	14	13	11	11	7	6	6	6	5	5
35/	114	4	6	6	6	5	5	3	3	2	2	2	2	2
36/	14	14	3	3	3	3	3	3	2	2	2	2	2	2
37/	17	17	1	1	1	1	1	0	0	0	0	0	0	0
38/	18	17	4	4	4	4	4	4	4	3	3	3	3	2
39/	7	17	2	2	2	2	2	2	2	2	2	2	2	2

Table 5 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
40/	15	15	2	2	2	2	2	2	2	2	2	2	2	2
41/	83	100	2	2	2	2	2	2	2	2	1	1	1	1
42/	104	190	1	1	1	1	1	1	0	0	0	0	0	0
43/	38	80	2	2	2	1	1	0	0	0	0	0	0	0
44/	40	80	4	4	4	4	4	4	4	3	3	3	2	2
45/	43	80	4	4	4	4	4	3	2	2	2	2	2	2
46/	60	80	2	2	2	2	2	2	2	2	2	2	2	2
47/	63	80	2	2	2	2	2	2	2	2	1	1	1	1
48/	64	80	3	3	3	3	3	3	3	2	2	2	2	2
49/	67	80	14	14	14	14	14	9	8	8	7	6	6	5
50/	75	80	8	6	6	5	4	4	4	2	2	2	2	2
51/	76	80	4	3	3	2	2	2	1	1	1	1	1	1
52/	99	80	4	4	4	4	4	4	4	4	2	2	2	2
53/	151	80	2	2	2	2	2	2	2	2	2	2	2	2
54/	4	82	4	4	4	4	4	4	4	3	2	2	2	1
55/	26	82	8	8	8	8	7	5	3	2	2	2	2	2
56/	68	82	6	6	6	3	3	2	2	2	2	2	2	2
57/	77	82	6	4	4	4	4	4	4	3	3	3	3	3
58/	69	84	6	4	4	4	4	4	4	4	4	2	2	2
59/	100	84	2	2	2	2	2	2	1	1	0	0	0	0
60/	17	84	2	2	2	2	2	2	2	2	2	2	2	2
61/	90	87	1	1	1	1	1	1	1	1	0	0	0	0
62/	16	87	1	1	1	0	0	0	0	0	0	0	0	0
63/	90	90	4	4	4	3	3	3	0	0	0	0	0	0
64/	2	90	1	1	1	1	1	0	0	0	0	0	0	0
65/	3	90	1	1	1	1	1	1	1	1	1	1	1	1
66/	4	90	1	1	1	1	1	1	1	1	1	1	1	1
67/	61	90	1	1	1	1	1	1	1	1	1	1	1	0
68/	100	3	3	3	3	3	2	2	2	2	1	1	1	1
69/	160	4	2	2	2	2	2	1	1	1	1	1	1	1
70/	40	14	1	1	1	1	1	0	0	0	0	0	0	0
71/	41	14	2	1	1	1	1	1	1	1	1	1	1	1
72/	112	17	2	2	2	2	2	2	2	2	2	2	2	2
73/	130	17	3	3	3	3	3	3	3	3	3	3	3	3
74/	149	17	2	2	2	2	2	2	2	1	1	1	1	1
75/	160	17	6	4	4	4	4	3	2	2	2	1	1	1
76/	164	17	2	2	2	2	2	2	2	2	2	2	2	2
77/	165	17	4	2	2	2	2	2	2	1	1	1	1	1
78/	166	17	2	2	2	2	2	1	1	1	1	1	1	1
79/	169	17	2	2	2	2	2	1	1	1	1	1	1	1
80/	172	17	4	3	3	2	2	1	1	1	1	1	1	1
81/	83	17	1	1	1	1	1	1	1	1	1	1	1	1
82/	26	17	4	4	4	4	3	3	3	3	3	1	1	1
83/	24	17	2	2	2	1	1	1	1	0	0	0	0	0
84/	84	50	18	13	13	7	7	6	6	6	6	5	5	5
85/	87	53	8	8	8	8	8	7	7	4	4	4	4	4
86/	24	6	1	1	1	0	0	0	0	0	0	0	0	0
87/	30	6	1	1	1	1	1	0	0	0	0	0	0	0
88/	24	24	8	8	8	7	7	4	4	3	3	3	3	3
89/	16	24	8	8	8	7	7	3	3	2	2	1	1	1
90/	26	16	10	10	10	10	10	10	10	9	9	5	5	5
91/	27	16	5	5	5	5	5	4	4	4	4	3	3	2
92/	114	114	1	1	1	0	0	0	0	0	0	0	0	0

Table 5 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
93/	132	132	4	4	4	4	4	4	4	4	4	3	3	3
94/	26	26	10	10	10	8	8	8	8	6	6	4	4	4
95/	30	30	23	23	23	23	23	23	23	22	22	21	21	20
96/	21	100	1	1	1	1	1	1	1	1	1	1	1	1
97/	61	100	1	1	1	1	1	1	1	1	1	1	1	1
98/	65	160	2	2	2	2	2	2	2	1	1	1	1	1
99/	62	62	2	2	2	2	2	2	2	2	2	2	2	2
100/	82	17	1	1	1	1	1	1	1	1	1	1	1	1
101/	86	86	1	1	1	1	1	1	1	1	1	1	1	1
102/	86	87	1	1	1	1	1	1	1	1	0	0	0	0
103/	100	59	2	2	2	2	2	2	2	2	2	2	2	2
104/	90	190	1	1	1	1	1	1	1	1	0	0	0	0
105/	243	80	3	3	3	3	3	3	3	3	3	3	3	3
106/	134	80	2	2	2	2	2	2	2	2	1	1	1	1
107/	100	132	1	1	1	0	0	0	0	0	0	0	0	0
108/	134	160	1	1	1	1	1	1	1	1	1	1	1	1
109/	18	1	2	2	2	0	0	0	0	0	0	0	0	0
110/	80	3	2	2	2	2	0	0	0	0	0	0	0	0
111/	201	83	2	2	2	2	2	1	1	1	1	1	1	1
112/	203	160	2	2	2	2	2	2	1	1	1	1	1	1
113/	62	80	8	0	0	0	0	0	0	0	0	0	0	0
114/	17	2	1	1	1	0	0	0	0	0	0	0	0	0
115/	45	80	10	10	10	10	9	8	8	7	7	5	5	5
116/	139	190	1	1	1	0	0	0	0	0	0	0	0	0
117/	160	190	2	1	1	1	0	0	0	0	0	0	0	0
118/	14	190	2	2	2	2	0	0	0	0	0	0	0	0
119/	82	80	10	8	8	7	3	2	2	2	2	2	1	1
120/	83	80	1	0	0	0	0	0	0	0	0	0	0	0
121/	91	80	1	1	1	1	1	1	1	1	1	1	1	1
122/	94	80	2	2	2	2	1	1	1	1	1	1	1	1
123/	101	80	1	1	1	1	1	1	1	1	1	1	1	1
124/	102	80	1	1	1	1	1	1	1	1	1	1	1	1
125/	103	80	1	1	1	1	0	0	0	0	0	0	0	0
126/	104	80	2	2	2	2	2	2	2	2	2	2	2	2
127/	233	80	12	12	12	12	10	8	8	7	4	4	4	4
128/	235	80	2	2	2	2	2	2	2	2	2	2	2	2
129/	236	80	2	2	2	2	2	2	2	2	2	2	2	2
130/	244	80	2	2	2	2	2	2	2	2	2	2	2	2
131/	245	80	2	2	2	2	2	2	2	2	2	2	2	2
132/	90	82	1	1	1	1	1	1	1	1	1	1	1	1
133/	99	82	2	2	2	2	2	2	2	2	1	1	1	1
134/	90	83	2	2	2	2	2	2	2	2	2	2	2	2
135/	94	83	1	1	1	1	1	1	1	1	1	1	1	1
136/	99	84	1	1	1	1	0	0	0	0	0	0	0	0
137/	100	100	1	1	1	1	1	1	1	1	1	0	0	0
138/	160	114	1	1	1	1	1	1	1	1	1	1	1	1
139/	115	115	3	3	3	3	3	2	2	2	1	1	1	1
140/	80	2	4	4	4	2	1	1	0	0	0	0	0	0
141/	83	4	4	4	4	4	2	2	1	1	0	0	0	0
142/	80	14	1	0	0	0	0	0	0	0	0	0	0	0
143/	160	16	1	1	1	0	0	0	0	0	0	0	0	0
144/	254	17	2	1	1	1	1	1	1	1	1	1	1	1
145/	255	17	2	1	1	1	1	1	1	1	1	1	1	1

Table 5 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
146/	28	16	1	1	1	1	1	1	1	1	1	1	1	1
147/	30	16	4	4	4	4	4	2	2	1	1	1	1	1
148/	6	17	2	2	2	2	2	2	2	2	2	2	2	2
149/	28	17	1	1	1	1	1	1	1	1	1	1	1	1
150/	41	17	2	2	2	2	2	2	2	2	2	1	1	1
151/	80	6	2	1	1	1	0	0	0	0	0	0	0	0
152/	82	38	2	2	2	2	2	2	2	2	2	2	2	2
153/	25	1	4	4	4	4	4	4	4	4	4	4	4	3
154/	87	21	1	1	1	0	0	0	0	0	0	0	0	0
155/	87	199	6	6	6	6	6	3	3	3	3	2	2	2
156/	82	200	2	2	2	2	2	2	2	1	1	1	1	1
157/	82	258	2	2	2	1	1	1	1	1	1	1	1	1
158/	80	206	6	6	6	5	3	3	3	3	3	3	2	2
159/	82	209	4	4	4	3	3	2	2	2	2	1	1	1
160/	22	1	3	3	3	3	3	3	2	2	2	2	2	2
161/	265	82	4	4	4	4	4	4	3	3	2	2	2	2
162/	157	157	1	1	1	1	1	1	1	1	1	1	1	1

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NUCLEOPHILIC SUBSTITUTION AT TETRACOORDINATED SULFUR ATOM. 1. REACTIVITY OF AMINES AND INORGANIC IONS

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The reactivity of amines and the $F^{\ominus}$, $OH^{\ominus}$, $HOO^{\ominus}$, $ClO^{\ominus}$ and $BrO^{\ominus}$ ions with respect to 4-nitrophenyl-4'-toluene-sulfonate in water at 25°C, the ionic strength μ = 1.0 (KCl) have been studied. The rate of aminolysis remarkably depends on the basicity of amines and it can be described by the Brønsted equation (β = 0.79). The reactivity of inorganic ions (except for the hydroxyl ion) has turned out to be abnormally high in these reactions. For the first time the existence of the α-effect of hydrobromite ion has been detected. A direct nuleohilic attack of the amines at the electron-deficient sulfur atom with breaking of the S-O bond of ether proved to take place.

The problem of finding such reagents which might effectively interact with the substrates stable in water as well as the ways of activation of these processes remains topical from both the practical as well as theorical points of view.[1] 4-nitrophenyl-4'-toluenesulfonate (NPTS) belong to such possible substrates. This kind of ether is resistant to the alkaline hydrolysis up to pH≈12, thus enabling to study the reactivity of compounds having relatively

high basicity during the experiments not depending on the pH. In case of this substrate the IR spectrophotometry can be used, which also favored the selection of the substrate as a model.

Literature data on the reactivity of nucleophiles with respect to the NPTS are rather scarce[2]. Nucleophilic reactivity of bases belonging to different classes with regard to the other sulfur-containing substrates (α-disulfones[3], cyclic ethers[4], sulfochlorides[5], etc.[6]) has also been touched upon in a limited number of reports. Besides, the reactions of various nucleophile classes have been studied under different experimental conditions complicating the general discussion of the nucleophility problem concerning the processes of substitution at the sulfonylic electrophilic center.

The present paper is aimed at studying the reactivity of a number of inorganic ions, primary, secondary and tertiary amines with regard to NPTS in water at 25°C, the ionic strength μ = 1.0 (KCl). Amines usually have a comparatively low reactivity and they do not participate actively in the decomposition of stable substrates[1]. Therefore the present reaction series can be regarded as a standard and consequently be taken as a bases for estimating the efficiency of action of various nucleophile classes.

Experimental Results

Reaction of 4-nitrophenyl-4'-toluenesulfonate (NPTS) with inorganic ions. Figs. 1 and 2 depict the IR spectra of NPTS, the products of a complete hydrolysis but also the character of changes of the NPTS IR spectra in time if pH = 13.00. The NPTS IR spectrum does not depend on the medium acidity (Fig. 1), though in alkaline solutions it remarkably varies in time (Fig. 2). The absorption increases if λ = 400 nm, while in acidic and neutral solutions the NPTS spectrum remained unchanged dor $\approx$ 10 days.

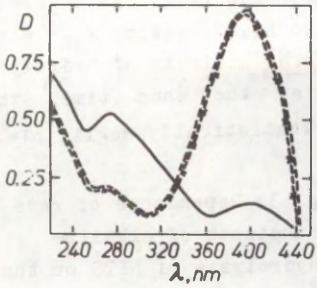

Fig. 1. IR spectra of NPTS (straight line if pH=1.68, 6.86, 9.18) and the products of a complete hydrolysis of NPTS (-x-x-) if pH= 13.00. Spectrum of 4-toluenesulfonic acid and 4-nitrophenole (pH=13.00) reference mixture (----) coincidss with that of the products of a complete hydrolysis of NPTS.

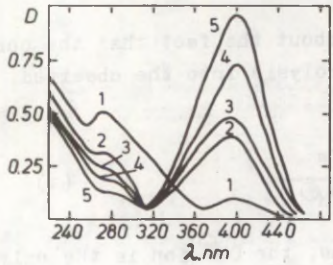

Fig. 2. Variation of IR spectra of NPTS in time t if pH=13.00; t(min): 0(1), 10(2), 20(3), 40(4), 60(5).

As the absorption level at 400 nm corresponds to that of 4-nitrophenolate ion, we can suggest that the variation character of the IR spectra in time is connected with the hydrolytic decomposition catalyzed by the hydroxyl ion. After termination of the hydrolysis, the IR spectra of reaction products coincide with that of the reference mixture, made up of toluenesulfonic acid and 4-nitrophenole (Fig. 1) as the expected products of the hydrolysis.Consequently, the NPTS alkaline hydrolysis proceeds quantitatively and irreversibly.

The rate of the alkaline hydrolysis is growing linearly if the hydroxyl ion becomes more active, not depending on the concentration of buffer components (Fig. 3). Procession of experimental results according to Eq.(1) yields $k_{OH^\ominus}$ = = 0.0080±0.0004, $M^{-1} \cdot s^{-1}$ (based on the activity of hydroxyl ion and not on its concentration), at the same time, the intercept on the ordinate axis is statistically negligible.*

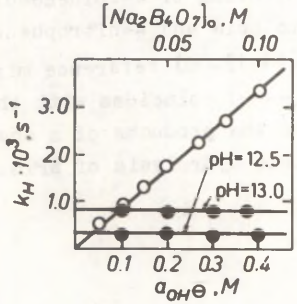

Fig. 3. Dependence of rate constants of alkaline hydrolysis of NPTS on the activity of hydroxyl ion (○) and on the concentration of buffer components (●, pH= const) in water at 25°C, μ = 1.0 (KCl).

The latter evidences about the fact that the contribution of the spontaneous hydrolysis into the observed rate constant is very small.

$$k_H = k_{OH^\ominus}\, a_{OH^\ominus} = k_{OH^\ominus} \frac{K_w}{a_{H^\oplus}} \qquad (1)$$

Consequently, in these conditions, the $OH^\ominus$ ion is the only reactive water component in case of the NPTS hydrolysis.

The reaction of NPTS in the presence of hydrogen peroxide was studied in a wide range of pH and initial concentration of $[HOOH]$. The reaction rate grows with the increase of $[HOOH]_o^o$ and pH, approaching the k_H close to the value critically independent of the medium (Fig. 4a).

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* The rate constant of the alkaline hydrolysis based on the $OH^\ominus$ ion concentration was obtained applying the activity coefficient $\gamma_{OH^\ominus} = 0.67^7$ and it is given in Table 1.

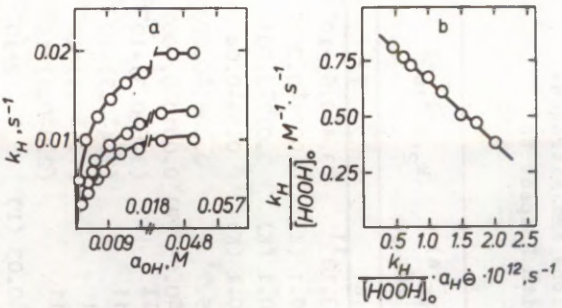

Fig. 4. Interaction of NPTS with hydroxide ion in water at 25°C μ = 1.0 (KCl).

a) Dependence of the rate constants k_H, s^{-1} on the activity of the hydroxyl ion (1- $[HOOH]_o$ = = $1.98 \cdot 10^{-2}$, M; 2- $[HOOH]_o$ = $1.48 \cdot 10^{-2}$, M; 3 - $[HOOH]_o$ = $9.9 \cdot 10^{-3}$, M).

b) Processing of kinetic results according to term (3) in the coordinates of the equation of Eadie ($[HOOH]_o$ = $1.98 \cdot 10^{-2}$ M).

If the reaction proceeds independently of the pH, its rate can be determined via the initial concentration of hydrogen peroxide only*. The $k_{HOO^\ominus}$ = 1.00±0.05, $M^{-1} \cdot s^{-1}$ was calculated from the limiting values of k_H:

$$k_H = k_{HOO^\ominus}[HOO^\ominus]_o = k_{HOO^\ominus}[HOOH]_o \qquad (2)$$

In the region of the pH-dependent decomposition, the process rate is determined both by the acidity of the medium and the reagent's concentration (Fig. 4a), i.e. it can be expressed as:

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* Conditions for conducting the experiment were chosen so that the contribution of alkaline hydrolysis did not exceed 5%.

Table 1

Conditions of Condacting the Experiment, Basicities of Inorganic Ions and Nitrogen-Containing Nucleophiles (pK_a) and Their Reactivity ($k_2, M^{-1} \cdot s^{-1}$) with Respect to NPTS in Water, at 25°C, μ = 1.0(KCl)

No	Nucleophile	pH	Nucleophile concentration M	Total number of experiments	pK_a a)	$k_2, M^{-1} \cdot s^{-1}$
1	2	3	4	5	6	7
1.	Fluoride ion	8.04	0.25-0.75	3	3.18[11]	$(3.4 \pm 0.6) \cdot 10^{-7}$
2.	Hypochlorite ion	7.59-11.79	0.041-0.2	6	7.4±0.1 (K)	0.0091±0.0005
3.	Hypobromite ion	8.99-12.29	0.0021-0.034	9	8.7±0.1 (K)	0.017±0.001
4.	Hydroperoxide ion	10.99-12.69	0.005-0.04	30	11.5±0.1 (K)	0.99±0.04
5.	Hydroxyl ion	12.74-13.58	0.055-0.42	16	15.7[1]	0.0080±0.0003
6.	Piperidine	11.43-11.49	0.15-0.8	6	11.42±0.05 (P)	0.0010±0.0007
7.	Dimethylamine	10.77-11.40	0.2-0.8	6	10.77[11]	$(3.6 \pm 0.3) \cdot 10^{-4}$
8.	Diethylamine	10.93-11.30	0.2-0.8	5	10.93[11]	$(2.4 \pm 0.5) \cdot 10^{-4}$
9.	n-Butylamine	10.45-11.30	0.3-1.0	6	10.7[11]	$(1.5 \pm 0.1) \cdot 10^{-4}$
10.	Ethylamine	10.63-11.00	0.2-0.8	10	10.63[11]	$(2.8 \pm 0.4) \cdot 10^{-4}$
11.	N-Methylpiperidine	10.68-12.07	0.1-0.8	9	10.45±0.03 (P)	$2 \cdot 10^{-5}$
12.	Piperazine	10.00-10.76	0.26-0.8	8	9.90±0.05 (P)	$(2.8 \pm 0.1) \cdot 10^{-5}$ $1.4 \cdot 10^{-5}$ b)
13.	Glycine	9.68-10.72	0.3-0.0	11	9.68±0.04 (P)	$(2.7 \pm 0.2) \cdot 10^{-5}$

Table 1 continued

1	2	3	4	5	6	7
14.	4-Aminopyridine	10.06-10.11	0.4-1.0	5	9.28 ± 0.04 (P)	$(3.8 \pm 0.1) \cdot 10^{-5}$
15.	Morpholine	8.77-10.18	0.4-1.0	10	8.77 ± 0.05 (P)	$(2.8 \pm 0.2) \cdot 10^{-5}$
16.	Hydrazine	9.18-9.25	0.3-1.5	7	8.2 [11]	$(7.6 \pm 0.7) \cdot 10^{-5}$ $(3.8 \cdot 10^{-5})$ b)
17.	Tris	9.25-9.37	0.4-0.8	4	8.1 [11]	$(1.1 \pm 0.2) \cdot 10^{-6}$
18.	N-Methylimidazole	8.40	0.6-1.0	3	7.33 [1]	$(5.8 \pm 0.1) \cdot 10^{-7}$
19.	Imidazole	8.39-8.46	0.6-1.0	3	7.24 ± 0.2 (P)	$(5.1 \pm 0.2) \cdot 10^{-7}$
20.	Hydroxylamine	9.07-9.26	0.5-1.5	12	6.0	0.00013 ± 0.00001

Note. a) Ionization constants have been determined kinetically (K) and potentiometrically (P).

b) Corrected by the statistical factor equalling 2.

$$k_H = k_{HOO^\ominus} [HOOH]_o = k_{HOO^\ominus} [HOOH]_o \alpha =$$

$$= k_{HOO^\ominus} \cdot \frac{K_a}{K_a + a_{H^\oplus}} [HOOH]_o , \qquad (3)$$

where $\alpha = K_a/K_a + a_{H^+}$ is the contribution of the $HOO^\ominus$ ion at the given pH value. Treatment of the equation in the coordinates of the Eadie[8] term (Fig. 4b) enables us to calculate not only $k_{HOO^\ominus} = 0.99 \pm 0.04$, $M^{-1} \cdot s^{-1}$ but also the constant of acidic ionization of hydrogen peroxide $pK_a = 11.4 \pm 0.1$. Similarity of the $k_{HOO^\ominus}$ values measured under various experimental conditions, confirms the assumption that the $HOO^\ominus$ ion is the reactive form of hydrogen peroxide. A good correlation of the found and literature values of pK_a ($pK_a = 11.7$[9]) refers to the correctness of this technique.

In contrast to the alkaline hydrolysis, the rate of the NPTS reactions with the $HOO^\ominus$-ion depends on the nature of buffer components. In the phosphate and carbonate buffers the reaction rate remains practically unchanged, but in case of sodium tetraborate the k_H values considerably drop when the $[Na_2B_4O_7]_o$ increases. The higher the medium activity (Fig. 5), the lower the rate.

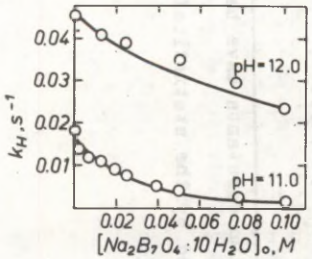

Fig. 5. Dependence of k_H values on the concentration of sodium tetraborate in case of NPTS reactions with hydroperoxide ion in water at 25°C, μ =1.0(KCl)

Such kind of influence of the components of sodium tetraborate can be caused by the equilibrium formation of the perborate anion in the reaction system, which reacts with the ethers of phosphoric and carboxylic acids[10]. The dependence of the k_H value on the $Na_2B_4O_7$ concentration is rather com-

plicated (Fig. 5), for that reason a detailed kinetic analysis of the reactions was not carried out. Still, it is evident that the reactivity of the perborate anion is smaller than that of hydroperoxide ion.

The NPTS reaction with sodium fluoride was studied in the conditions where the whole reagent was in the form of fluoride ion (pH=8.00, pK_a=3.18[11]). It enables to find its reactivity (see Table 1) according to the dependence "k_H- $[NaF]_o$".

It should be taken into account when studying the reactivity of the anions of hypobromic and hypochloric acids that these compounds does not act only as efficient nucleophiles splitting NPTS but they also demonstrate clear oxidizing properties. In Fig. 6 are given the anamorphoses, illustrating the variation of the absorption of the 4-nitrophenolate ion, forming in time in case of various pH values.

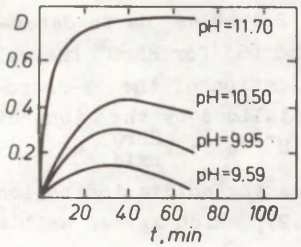

Fig. 6. Variation of optical density (λ = 400 nm) in time in case of the NPTS decomposition in water at 26°C, μ = 1.0 (KCl) ($[HClO_4]_o$= = 0.34, M; $[NPTS]_o \approx$ = $4 \cdot 10^{-5}$, M).

The rising section of the curves reflects the accumulation of 4-nitrophenolate ion connected with the NPTS decomposition, while the descending one shows its oxidation level[12]. The shift of the peaks of anamorphoses, their becoming more frequent in time and dropping of the D_{max} absolute values with the growth of the medium acidity speaks about the catalytic character of the 4-nitrophenolate ion oxidation. Studying of the 4-nitrophenol (NP) oxidation by means of hypohalogenic ions in independent experiments has shown that this

process is really subjected to a specific acidic catalysis (Table 2) but its rate can be described by equation (4):

$$k_H = k_{oxidizer} \cdot [H\,HalO] \cdot a_{H^+} \qquad (4)$$

where $[H\,HalO]$ denotes the equilibrium concentration of hypohalic acid at the given pH value.

Table 2

Interaction of 4-nitrophenole with Hypohalic Acids in Water at 25°C, μ = 1.0 (KCl)

$[HClO]_0$ = 0.01 M		$[HBrO]_0$ = 0.016 M	
pH	k_H, s^{-1}	pH	k_H, s^{-1}
6.95	0.082	9.44	0.054
7.07	0.053	9.57	0.033
7.27	0.025	9.95	0.0096
7.48	0.015	10.02	0.0078
7.52	0.014	10.20	0.0066
7.86	0.0037	10.40	0.0024
8.08	0.0015	10.55	0.0016

Treatment of the data given in Table 2 enables us to determine according to Eq. (5) for HClO and (6) for HBrO* the values of $k_{oxid.}$, characterizing the oxidation of the 4-nitrophenolate ion with hypohalic acids catalized by the ion of hydroxonium ($k_{oxid.}^{HClO} = (1.1\pm0.1)\cdot10^8$, $M^{-2}\cdot s^{-1}$; $k_{oxid.}^{HBrO} = (9.0\pm0.9)\cdot10^{10}$, $M^{-2}\cdot s^{-1}$) as well as the acidic ionization constant for HClO ($K_a^{HClO} = 10^{-(7.4\pm0.2)}$), which agrees well[11] with

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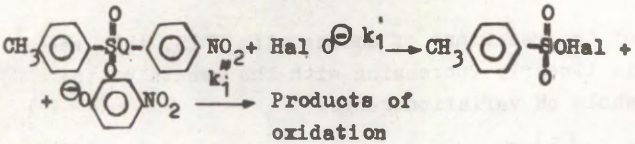
* At processing of the experimental data for HBrO, the value $K_a^{HBrO} = 10^{-8.7}$[11] was used according to (6):

relationship (6) was found from (4) taking into account that $a_{H^+} \ll K_a$.

$$\frac{k_H}{[HClO]_o a_{H^\oplus}} = k^{HClO}_{oxid.} - \frac{1}{K_a} \cdot \frac{k_H}{[HClO]_o a^2_{H^\oplus}} \qquad (5)$$

$$\frac{k_H}{[HBrO]_o} = k^{HBrO}_{oxid.} \cdot \frac{a^2_{H^\oplus}}{K_a} \qquad (6)$$

The obtained experimental values evidence about the fact that the interaction of NPTS with $ClO^\ominus$ and $BrO^\ominus$ ions is a step-wise process with a variation of the rate determining stage if the medium acidity is varied (Scheme 7).



(7)

As a result of the hypohalite attack, during the 1st reaction stage form the acylhalide and 4-nitrophenolate ion. During the 2nd stage the 4-nitrophenolate ion (4-nitrophenol) is oxidized by means of hypohydrohalic acids. In case of the $ClO^\ominus$ ion at pH < 8 (pH< 10.5 for $BrO^\ominus$ ion) it is the first stage that determines the rate, but in the alkaline solutions, the oxidation of NP is decisive from the point of view of rate, therefore, it is possible in these conditions to find the nucleophilic reactivity of the $ClO^\ominus$ and $BrO^\ominus$ ions by the ordinary methods (see above) (the corresponding constants are given in Table 1).

The $k_{HalO^\ominus}$ and $k_{oxid.}$ valuee obtained in the independent experiments, allow quantitatively estimate the time of reaching the D_{max} (t_{max}, s)[13] during the two successive processes:

$$t_{max} = \frac{\ln k_1'/k_1''}{k_1' - k_1''} \qquad (8)$$

where $k_1' = k_{HalO^{\ominus}} [HalO^{\ominus}]$, $k_1'' = k_{oxid} [HHalO] a_{H^{\oplus}}$.
The coinciding experimentally found t_{max} and calculated values evidence about the validity of Scheme (7).

Reaction of NPTS with amines. It is known[2] that in the aqueous ethanol the NPTS aminolysis proceeds in three parallel channels (8) : the amine nucleophilic attack (B) on the atom of sulfur (k_2, $M^{-1} \cdot s^{-1}$); general basic (k_B, $M^{-2} \cdot s^{-1}$) and generally acidic ($k_{BH^{\oplus}}$, $M^{-2} \cdot s^{-1}$) catalysis of nucleophilic substitution:

$$k_H = k_2 [B]_o \alpha + k_B [B]_o^2 \alpha^2 + k_{BH^{\oplus}} [B]_o^2 \alpha (1-\alpha) \qquad (9)$$

where α is the contribution of the amine being in basic form.

In case of the reactions of amines with NPTS, the reaction rate is linearly increasing with the growth of the $[B]_o$ in the whole pH variation range:

$$k_H = k_2 [B]_o \alpha \qquad (10)$$

Consequently, the decomposition catalysis of NPTS by acidic and basic components cannot be detected. In case of hydrazine, the reaction order decreases with the increase of $[NH_2\text{-}NH_2]_o$ if pH= const. This must be connected with the association of the amine[7] and therefore the k_2 values were taken in the linear region of the dependence, presented in Fig. 7.

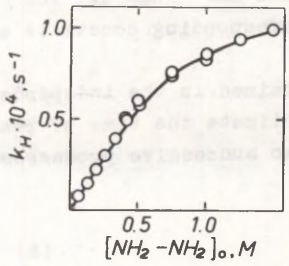


Fig. 7. Dependence of the k_H values on the $[NH_2\text{-}NH_2]_o$ for the NPTS reactions with hydrazine in water at 25°C, μ = 1.0 (KCl), pH=9.20.

The aqueous solutions of azoles which are not substituted as for the NH group, contain three types of particles: the cationic (I), neutral (II) and anionic (III) forms:

(11)

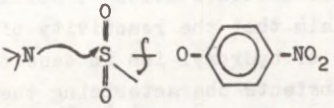
Both neutral and anionic forms of azoles can react with NPTS. If pH=8.4, the reactivity of imidazole practically coincides with that of N-methylimidazole (Table 1). It means that the contribution of the interaction of azole anion with ether into the given reaction rate is negligible in comparison with that of the flow, where the neutral molecule of imidazole acts as a reacting form. This cannot be a surprise, as far as the contribution of the anionic form at pH=8.4 is very small ($\alpha_{III} \approx 10^{-6}$). In order to make the contribution of the flow more substantial, the reactivity of the anionic form of azole must exceed that of a neutral molecule $\approx 10^6$ times. Unfortunately, we could not detect the interaction of the anionic forms of imidazole. 4(5)-phenyl-imidazole and benzimidazole up to pH=13.5, although the initial buffer concentration reached the values ensuring the equality of concentrations of the azole anions and hydroxyl ion. The observed rate constants of pseudofirst order will drop if the initial buffer concentration[7] increases, the section $k_H = (2.0 \pm 0.3) \cdot 10^3$, s^{-1} intersected at the axis of ordinates, corresponding to the alkaline hydrolysis at pH = 13.4, i.e. practically the azoles do not catalyze the NPTS decomposition, on the contrary, they tend to inhibit it. This is quite an unexpected fact, since it is known that the anionic forms of azoles act as effective nucleophilic reagents in case of the ethers of phosphoric[14] and carbolic acids[15]. Still, the data obtained enable us to claim that the reactivity of azole anions is lower than that of hydroxyl ion in case of NPTS. The second order rate constants characterizing their reactivity hardly ever exceed $k_2 \approx 10^{-3}$, $M^{-1} \cdot s^{-1}$, i.e. they react with ether even slower than the studied amines. At the present moments it is difficult to explain such an unexpected

behavior of azole anions in the given reaction. The problem should be given a special study.

Discussion of Results

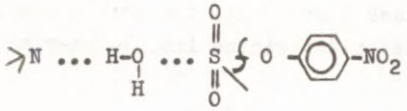
Decomposition of esters of sulfonic acids can include the amine attack either on the aromatic carbon atom of the benzene nucleus or on the electron-deficient sulfur atom[8,16]. The nature of bond breaking depends on the following factors: The nature of a leaving group, the reagent's nucleophility, the structure of the acyl part of the molecule of ether, etc.[8,16]. In case of NPTS, the authors of[2] suppose on the bases of the quantitative yield of 4-nitrophenolate ion that there is no amine attack on the aromatic atom of carbon there. In our opinion, such an approach is not enough well-founded to prove the breaking character, as far as the products of substitution at the aromatic centers of carbon and 4-nitrophenolate-ion are absorbed in the same region. Our method seems to be more general (cf.[17]): by termination of the NPTS reaction with the nucleophiles containing nitrogen and the acidification of the medium up to pH ≈ 3, the absorption at λ = 400 nm equals practically zero in case of the whole set of amines* studied. It can be confirmed that the reaction product is 4-nitrophenol and also the breaking of the S-O bond takes place.

The mechanism of the S-O bond breaking can include the following steps: a) the amine nucleophilic attack on the sulfur atom with the formation of sulfonylamide (12), or b) general basic amine assistance to the hydrolytic decomposition of NPTS by means of the water molecules with water, the 4-toluenesulfonic acid being the reaction product (13).



(12)

* No absorption was observed in case of the anionic forms of azoles thus excluding their possible attack on the aromatic atom of carbon.



(13)

These two possible breaking mechanisms of the S-O bond (despite their stoichiometrically different transition states) are kinetically indistinguishable and the choice between (12) and (13) can clearly be made only if the reaction products are known. The quantitative formation of sulfonylamides in the NPTS reaction with piperidine and imidazole whose basicities totally differ ($\approx 10^4$ times) proves the validity of a direct nucleophilic attack on the sulfur atom. However, it is impossible to determine the reaction products in case of such tertiary amines as N-methyl-imidazole and 4-aminopyridine, since the forming sulfonylamine cations are not stable and they undergo a further hydrolytic dissociation. The only way to prove the existence of the reaction mechanism in this case is to analyze the "structure - reactivity" relationship as well as to study the deuterium isotopic effect of the solvent.

The values of k_2 and pK_a for the whole set of reagents studied in the report are summed up in Table 1. In Fig. 8 is given the Brønsted plot for amines.

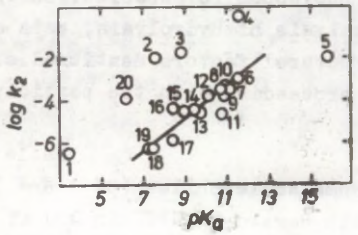


Fig. 8. The Brønsted plot for reactions of amines and inorganic ions with NPTS in water at 25°C, μ=1.0 (KCl). The numbers coincide with those of Table 1.

The straight line passes through all the points (hydrazine, hydroxylamine and N-methylpiperidine incl.), obeying the equation:

$$\log k_2 = (-11.9 \pm 0.7) + (0.79 \pm 0.07) pK_a, \qquad (14)$$

$$r = 0.97,\ S_{total} = 0.31,\ N = 11$$

The existence of the common Brønsted dependence in case of the primary, secondary and tertiary amines refers to the identical bond breaking mechanism. The direct nucleophilic attack on the sulfur atom is in agreement with the high $\beta = 0.79$ value and with the absence of the deuterium isotopic solvent effect in case of 4-aminopyridine and piperidine (Table 3). In case of a number of amines, the log k_2 values' both positive and negative deviations from the Brønsted equation are observed. In case of morpholine, the growth of reactivity is insignificant ($\Delta = +0.47$) but in case of hydroxylamine and hydrazine, their substantial positive deviations ($\Delta = +3.3$ and $\Delta = +1.04$, respectively) can be explained by the α-effect. The negative deviations of trioxymethylaminomethane ($\Delta = -0.42$) and N-methylpiperidine ($\Delta = -1.0$) are evidently caused by great steric hindrance during the attack on the sulfonylic atom of sulfur. Such scattering of points in the graph 'reactivity - pK_a' is also more in keeping with the mechanism of nucleophilic substitution than with that of general basic catalysis of hydrolysis, as a smaller susceptibility to the structural factors mentioned above is peculiar to the processes proceeding with the participation of general basic catalysts.

Table 3

Basicity of Some Nucleophiles (pK_a) and Their Reactivity (k_2, $M^{-1} \cdot s^{-1}$) with Regard to NPTS in D_2O at 25°C, μ=1.0(KCl)

No	Nucleophile	pK_a (D_2O)	$k_2, M^{-1} \cdot s^{-1}$	$\frac{k_2(H_2O)^a}{k_2(D_2O)}$
1.	4-aminopyridine	10.22 ± 0.04(P)[b]	$(3.0 \pm 0.3) \cdot 10^{-5}$	1.23
2.	Piperidine	12.11 ± 0.06(P)[b]	$(9.1 \pm 0.6) \cdot 10^{-4}$	1.11
3.	$OD^{\ominus}$	16.6[c]	$(9.9 \pm 0.2) \cdot 10^{-3}$	0.83

Notes.

[a] Variation of reactivity during the transtion from H_2O to D_2O

[b] The pK_a values ((D_2O) have been determined potentiometrically.

[c] Found from K_a (D_2O) =

$$= [D^{\oplus}][OD^{\ominus}]/[D_2O] = 10^{-14.87}/50.$$

Inorganic ions form a special group of nucleophiles. The interpretation of the mechanism of the alkaline hydrolysis tends to be rather complicated, since the reaction products do not permit to find out the site of the attack. Still, most probably the observed rate of the alkaline hydrolysis cannot be explained by the substitution at the aromatic carbon atom because in the case of such substrates as p-nitrochlorobenzene[7,17], p-nitrophenylmethylphosphonate-monoamine[18] and p-nitrophenylphosphatedianion[7,17] with which really takes place the $OH^{\ominus}$ ion attack on the aromatic atom of carbon, the reaction rates are negligible (10^{-7}-10^{-9}, $M^{-1}.s^{-1}$), i.e. in case of NPTS seems to be realized the nucleophilic substitution at the tetracoordinated sulfur atom. The fact that the $OD^{\ominus}$ and $OH^{\ominus}$ ion react with the comparable rates (see Table 1, No 5 and Table 3, No 3) is in keeping with this conclusion.

The remarkable negative deviation of log k_2 in case of hydroxyl ion from the correlation dependence for the amines cannot be explained by the difference between the solvation effects of the amines and $OH^{\ominus}$ ion, as far as the reagents must to a certain extent get desolvated both during proton addition as well as during the formation of transition state in which the attacking nucleophile will obtain a large positive charge. Therefore one of the reasons of the point's negative deviation in case of the hydroxyl ion is the fact that the growth of the $OH^{\ominus}$ ion basicity in the order of nucleophile studies anticipates the increase of its reactivity. The high value of the Brønsted slope (β = 0.79) leads to the negative deviation at the relationship "reactivity-basicity", i. e. it is more correct to speak about the abnormally high basicity of the hydroxyl-ion here and not about its smaller reactivity.

Similar deviations in case of the $OH^{\ominus}$ ion at high β values have been reported not only in case of the reactions with amines but also in case of the alkoxy-ions[19,20].

In contrast to the hydroxyl ion, in case of amines, the F^-, HOO^-, ClO^- and Br^- ions undergo remarkable positive deviations from the correlation "reactivity - basicity", revealing supernucleophilic properties in the dissociation reactions of NPTS. Thus, the hydroperoxide ion reacts 1000 times faster than piperidine, regardless of their practically coinciding basicities. The differences between the rates of the ClO^- ion and N-methylimidazole are still greater ($\approx 10^4$ times, cf. the pK_a values in Table 1). We also succeeded for the first time in establishing the abnormally high reactivity in case of the hypobromite ion ($\Delta = +3.3$).

As follows from Fig. 8, there is a certain interdependence between the reactivity and basicity of inorganic ions: the increase of the pK_a brings about the growth of the reaction rate. This cannot be an unexpected fact, it is most likely to reflect the common nature of the reaction center in these compounds: the $ClO^{\ominus}$, $HOO^{\ominus}$ and $BrO^{\ominus}$ ions contain a negatively charged oxygen atom, although the fluoride ion ($\Delta = +2.69$) also tends to the general relationship. At the same time it is quite clear that basicity is not the only factor determining the reactivity of the $HOO^{\ominus}$, $ClO^{\ominus}$, $BrO^{\ominus}$ and $F^{\ominus}$ ions. For instance, the hypobromite ion having a 20 times stronger basicity than the hypochlorite ion, reacts with NPTS only twice faster . These inorganic ions, the $BrO^{\ominus}$ ion incl., belong to the so called α-nucleophiles. As the task of the report was not to analyze the nature of the α-effect in a detailed way. We might only point out that the unusual reactivity of the α-nucleophiles in the first approximation can be explained by the following reasons: a) the absence of steric hindrance , b) the abnormally small basicity, c) the existence of the factors stabilizing the transition state, etc.[21] The $HOO^{\ominus}$ - and $ClO^{\ominus}$ ions reveal an increased reactivity with the substrates containing various

electron - deficient centers, while the $F^{\ominus}$ ion seems to have a special affinity to the tetracoordination atoms of sulfur[22] and phosporus[22]. Thus, having a smaller ($\approx 10^4$ times) basicity than imidazole, the $F^{\ominus}$ ion reacts with the NPTS only $\approx$1.5 times slower than imidazole. The abnormally high reactivity of the fluorine ion with respect to NPTS is evidently connected with the existence of strong resonant interactions between the sulfur and fluorine atoms in the transition state of the reaction, having a remarkable stabilizing effect on them thus increasing the nucleophility of the fluorine ion.

The point for hydroxylamine (Δ = +3.3) has practically the same positive deviation from the Brønsted relationship as the inorganic ions, belonging to the anionic oxygen-containing nucleophiles. The latter refers to the identical nature of the reaction center. In aqueous solutions, hydroxylamine can have either the form of a neutral molecule (IV) or that of a bipolar ion (V):

$$NH_2OH \rightleftharpoons \overset{\oplus}{N}H_3O^{\ominus}$$

IV V

If the neutral nitrogen atom in molecule (V) acts as the reaction center, no anomalies in the hydroxylamine reactivity are detected[23].

The mechanism of the NPTS reactions with inorganic ions is most probably similar with that of the amines: a direct nucleophilic attack on the sulfur atom is observed. It is confirmed by numerous examples of proceeding of the reactions of nucleophilic substitution at the unsaturated centers, i.e. the atoms of phosporus, carbon and sulfur[3,21]. At least for the $HOO^{\ominus}$, $ClO^{\ominus}$ and $BrO^{\ominus}$ ions any cases of acid-basic dissociation catalysis of the ethers containing the above-mentioned electron-donor centers were not found. Moreover, the $HOO^{\ominus}$ and $ClO^{\ominus}$ ions have the abnormal reactivity towards the substrates with the saturated carbon atom, in the case of which the general acidic-basic catalysis is not typical.

Experimental

Synthesis and Purification of Compounds. All nitrogen-containing nucleophiles except for 1-methylimidazole, 1-methylpiperidine and 4(5)-phenylimidazole were commercial compounds and were purified according to the standard methods. 1-methylimidazole and 1-methylpiperidine were prepared via the alkylation of imidazole[24] and piperidine[25]. It was purified by a multiple distillation in the nitrogen current. 4(5)-Phenylimidazole was obtained by means of the phenacylbromide condensation with formamide[26].

The inorganic extra pure and chemically pure reactives were applied without an additional purification. The hypochloric acid which did not contain the Cl_2 and $Cl^{\ominus}$ ion was synthesized according to[27]. In order to avoid dissociation, it was kept at -10-(-15)°C. The sodium hypobromite was obtained according to[27].

Heavy water (D_2O) and the solutions of deuterium chloride in D_2O, whose content of an isotope-substituting compound was 99.8% were used without purification; the sodium and potassium deuterooxides were prepared as recommended in[28].4-Aminopyridine was recrystallized from D_2O 2-3 times and dried in nitrogen atmosphere. The substitution of oxygen for deuterium in piperidine was carried out according to[29]. The volume completeness of isotopic exchange was controlled by means of the IR spectroscopy in the frequency range of the NH-group oscillation.

4-nitrophenol-4'-toluenesulfonate was synthesized and purified according to method[6].

Isolation of Reaction Products.

N-(4-Toluenesulfonyl)piperidine. 0.01 M NPTS in 10%-alcohol was added to the 1M piperidine solution in 10% alcohol (pH=11.4) at 50°C, mixing intensively. By the termination of the reaction, the excess of piperidine and solvents was evaporated in an rotational evaporator to its minimal volume. The precipitate was filtrated and recrystallized from the

ethanol-water mixture. A quantitative yield of the product was obtained. The melting point was 74-70°C, λ_{max}=230.9 nm.

N-(4-Toluenesulfonyl)imidazole. N-(4-toluenesulfonyl) imidazole was obtained similarly with that of the piperidine sulfonylation.The reaction mixture was acidified to pH≈3 and the solvent was distilled after that the oil separating out was extracted with ether, ether was distilled dry, the reaction products were treated with the 0.01 M soda solution and evaporated to their minimal volume. The oil was separated out and recrystallized from the ethanol-water mixture after its hardening. The yield was a quantitative one. The melting point was 94-96°C, λ_{max}=235.8 nm

The melting point and λ_{max} values of 4-toluenesulfonylamide coincide with those obtained in case of the products synthesized from 4-toluenesulfochloride and the corresponding amine.

Technique of Kinetic Measurements

The solutions of nucleophilic reagents were prepared with distilled water (with a 5% addition with respect to the ethanol volume) just before each series of kinetic measurements. The initial concentrations of nucleophiles enabled the reagent's solutions to be simultaneously also the buffer solutions. The ionic strength of the solutions was taken by conducting the 1M KCl. In case of the hypochloric acid, hypobromite and hydrogen peroxide, first were determined the initial concentrations of HClO, HBrO and HOOH (iodometrically[30] and permanganometrically[30], respectively), then the ionic strength was fixed*. In all experiments, the necessary pH values of buffer solutions were found by means of the concentrated NaOH and HCl solutions.

The reaction was monitored spectrophotometrically according to the 4-nitrophenole accumulation at λ =400-430 nm, applying a spectrophotometer "Specord UV VIS" at 25°C, The medium acidity was determined before and after each kinetic

* In order to keep a constant pH value, sodium dihydrophosphate and sodium carbonate were used in such cases.

test, if the pH variation after the experiment exceeded 0.05 pH units, the results were not taken into account. The initial NPTS concentration (4.10^{-5}M) in all kinetic tests was lower than that of the nucleophilic reagent (0.005-1.0M). The observed pseudofirst order rate constants were determined according to the variation of the optical density in time as follows:

$$\ln \frac{D_\infty - D_o}{D_\infty - D_t} = k_H \cdot t \qquad (14)$$

where D_o, D_t and D_∞ denote the optical densities at time moments $t=0, t=t_i$ and by termination of the reaction.

The oxidation of 4-nitrophenole with hypohalogenic ions was studied spectrophotometrically. The reaction rate was monitored by the excess of the 4-nitrophenolate ion at λ = = 400 nm, the rate constants were calculated from correlation (14).

Determination of Ionization Constants of Nucleophilic Reagents.

Ionization constants were determined at the ionic strength equalling 1.0 (KCl) either potentiometrically or kinetically[11]. In case of finding the ionization constants in heavy water, the 0.1 M DCl (or KOD) solutions were used as the titrator. The $pK_a(D_2O)$ values were calculated according to the equation:

$$pK_a(D_2O) = pD + \log \frac{[DA] + a_{OD}\ominus}{[A\ominus] - a_{OD}\ominus} \qquad (15)$$

where $pD = -\log a_D\oplus$, $a_{OD}\ominus$, denote the activity of the deuterooxylic ion. The pD values were calculated from the pH found experimentally and the temperatures according to the equation suggested in[28]:

$$pD = \text{"pH"} + (0.410 - 0.0002\, t^\circ), \qquad (16)$$

$a_{OD}\ominus$ was found from

$$a_{OD}\ominus = K_D/10^{-pD}, \qquad (17)$$

where K_D is the constant of the ionic product in case of D_2O.

The accuracy of the pK_a and k_H values was estimated by means of the statistics of small samples. Linear equations were treated by the least squares method.

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THE PRIMARY KINETIC SALT EFFECT ON INTERIONIC REACTIONS

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The nature of the primary salt effect on the rate constants of the interionic reactions is discussed on the basis of the structural theory of electrolyte solutions and Brønsted - Bjerrum principle. The corresponding formula for the salt effect on the different reaction types are given, and the verification of these in the variety of reactions and electrolyte concentration in the solution is made. The validity of this theory is demonstrated in the case of the interionic reactions with no side effects (i.e. ionic association or specific ion effects).

In the previous communication[1], a theoretical approach to the primary salt effect of the acid-base equilibria was proposed on the ground of the Brønsted - Bjerrum principle and the structural theory of strong electrolyte solutions. This article deals with the extension of this work on the chemical kinetics data.

According to the Brønsted[2] and Bjerrum[3], the observable rate constant k of the reaction

$$A + B + C + \ldots \longrightarrow [ABC\ldots]^{\neq} \qquad (1)$$

is given as

$$k = k_0 \cdot \frac{f_A \cdot f_B \cdot f_C \cdots}{f^{\neq}} , \qquad (2)$$

where k_o denotes the rate constant at the standard conditions (infinite dilution), and f_A, f_B, f_C,... and $f^{\neq}$ are the activity coefficients of the corresponding reagents and the transition complex $[ABC...]^{\neq}$, respectively. In the simple structural theory of solutions[4-6], the activity coefficient of ionic constituents is presented in the following form:

$$\ln f_i = -\frac{(ze)^2 \varkappa}{4\varepsilon RT} + 2 \cdot V_s c = -\frac{12464 \cdot 2\, z^2}{\varepsilon T} \sqrt[3]{\nu c} + 2V_s c \,, \quad (3)$$

where z and e are the ionic charge and elementary charge, respectively, $\varkappa$ is the specific parameter dependent on the electrolyte type and concentration in solution, ε is the macroscopic dielectric constant of the solvent, R - is the universal gas constant, T- temperature (^oK) and c - the molar concentration of the electrolyte in the solution. The parameter V_s is the characteristics for the solvent structure change in the volume[4] adjacent to a given ion and ν is the number of ions in the electrolyte molecule. Therefore, Eq. (3) can be rewritten as:

$$\ln f_i = a_t \sqrt[3]{c} + b_i c \quad (4)$$

or in the scale of decimal logarithms as:

$$\log f_i = \frac{a_t}{2.303} \sqrt[3]{c} + \frac{b_i}{2.303} c = a_t' \sqrt[3]{c} + b_i' c \,, \quad (5)$$

where a_t and a_t' are the theoretical constants at the given temperature and solvent for the particular ion charge type, and b_i and b_i' - the parameters individual for every ion in the solution of electrolyte.

For the activity coefficient of the electroneutral species f_n in the electrolyte solutions the following formula is valid[4]:

$$\ln f_n = 2V_s c = b_n \cdot c \quad (6)$$

or

$$\log f_n = \frac{b_n}{2.303} \cdot c = b_n' c \quad (7)$$

where V_s has the same meaning as in Eq.(3) and b_n is the characteristic constant for a given species and electrolyte.

Now it is comparatively simple to obtain the final equations for the rate constants of the different interionic reactions in the electrolyte solution by the substitution of Eqs. (4-7) into the Brønsted-Bjerrum formula (2). In the further discussion we proceed the verification of these formula on the ground of the variety of experimental data given by different authors.

1. The reaction between an ion and an electroneutral substrate:

$$A^+ + B \longrightarrow \qquad (8)$$

or

$$A^- + B \longrightarrow \qquad (9)$$

In this case

$$\ln k = \ln k_o + \Delta b \cdot c \,, \qquad (10)$$

where

$$\Delta b = b_{A^\pm} + b_B - b^{\neq}, \qquad (11)$$

(the subscripts $A^\pm$, B correspond to the respective reagents and the superscript $\neq$ denotes the transition complex) is the specific parameter for the given reaction and electrolyte in solution. There is a vast number of examples described in literature[8-17], where the rate constant of the reaction of this type obeys equation (10). Respectively, the contribution due to the electrostatic interionic interaction in the overall rate constant of the process (8) or (9) is zero effectively.

The structural dependence of the Δb-parameter on both the reagents and additional electrolyte in solution needs a special discussion. However, it has been shown[7] that the specific volumes V_s which are essentially determining the value of Δb, are not simple additive parameters but consist of the cross-terms between the structurization constants of different constituents in solution. The examples, where the Δb of a given reaction is linearly related to the V_s- values of pure electrolytes, are known (cf. Fig.1).

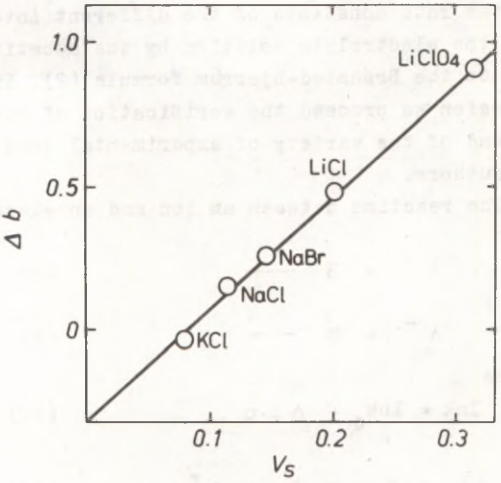
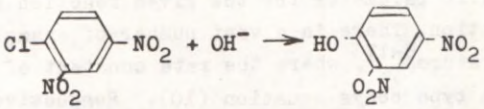


Fig. 1. The linear relationship between the Δb parameter of reaction [14]



and the specific volumes V_s [2] of the corresponding additional electrolytes in aqueous solutions.

2. Reactions between the simple oppositely charged ions:

$$A^{z_+} + B^{z_-} \longrightarrow [AB]^{(z_+ + z_-)^{\neq}} \qquad (12)$$

In this case the logarithm of the rate constant obeys the following equation:

$$\ln k = \ln k_o + a_t\left[(z_+^2 + z_-^2) - (z_+ + z_-)^2\right] \sqrt[3]{c} + \Delta b \cdot c =$$

$$= \ln k_o - 2z_+ z_- a_t \sqrt[3]{c} + \Delta b \cdot c \ , \qquad (13)$$

where z_+ and z_- are the ionic charges for cationic and anionic reagent, respectively and the parameter Δ b has the same general meaning as in formula (11). Many excellent measurements of the primary salt effect on the reactions of this type have been made by V.V. Sinev et al.[18-21] and other investigators. The results of the statistical data treatment according to equation (13) and the linearized equation

$$Y = \ln k + 2a_t z_+ z_- \sqrt[3]{c} = \ln k_o + \Delta b \cdot c \ , \qquad (14)$$

where the theoretically calculated interionic interaction term is substrated from the lnk value, are given in Table 1. Some instructive examples of the validity of simplified linearships

$$\ln k = \ln k_o - 2a_t z_+ z_- \sqrt[3]{c} \qquad (15)$$

in very dilute solutions, where the $\Delta b \cdot c$ term is negligible, are also given in Table 1. and in Fig. 2 and 3. In all cases studied here, the concentration of the ionic reagents is small in comparison with that of the additional neutral electrolyte and therefore the last term in Eq.(13) includes the $\Delta b \cdot c_{el}$ term only, where c_{el} is the concentration of an additional electrolyte. Otherwise this term becomes more complicated and has the additional parts $\Delta b' \cdot c_{A^+}$ and $\Delta b'' \cdot c_{B^-}$, where c_{A^+} and c_{B^-} are the respective concentrations of ionic reagents.

The overall fit of the experimental results with the theoretical equations is good (See reactions 1-10 in Table 1). Especially we mention the closeness of the experimental slope of the concentration cube-root dependence with its theoretical value (cf. columns 5 and 7 in Table 1). By no means the treatment presented in this work does not pretend to be the complete analysis of all salt effect data published during more than 60 years. However, the examples discussed here are the ones used especially for the demonstration of the Debye-Hückel electrostatic model validity in the primary salt effect description. The results obtained in this work yet confirm that in the dilute solutions, the structural theory of electrolytes is equally good, but in the wider range of elec-

trolyte concentrations it is either theoretically or experimentally more justified.

Finally, we should like to emphasize that the simple approach presented here is valid only in the case of a purely primary salt effect. The secondary effects (ion association or ion catalysis) which are quite common in the chemical kinetics in solution, especially in nonaqueous solvents lead to the much more complicated equations and need a special discussion.

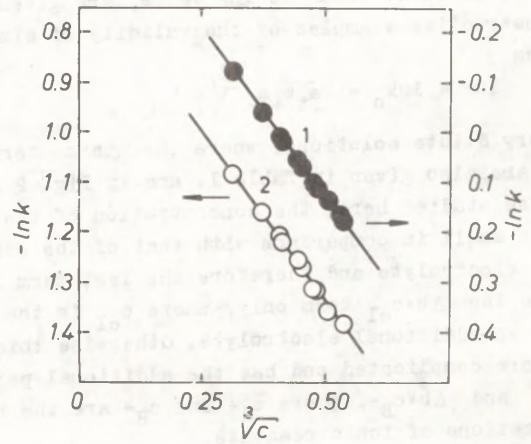


Fig. 2. The linear relationship between the lnk for the reactions[18,21]

$$R_1R_2R_3C^+ + OH^- \longrightarrow \quad (1)$$

and

$$R_1R_2R_3C^+ + CN^- \longrightarrow \quad (2)$$

and the cube-root of the overall electrolyte concentration in the solution. Straight lines correspond to the theoretical slopes.

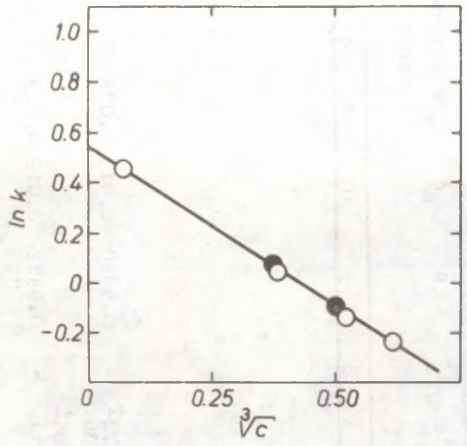


Fig. 3. The linear relationship between the lnk for the reaction[19]

$$R_1R_2R_3C^+ + OH^- \longrightarrow$$

and the cube-root of the overall electrolyte concentration in the solution. Straight line corresponds to the theoretical slope. Notations: ○ -KCl addition, ● - $NaNO_3$ addition.

3. Reaction between the like-charged ions.

This is quite a rare case, because the electrostatic repulsion between the like-charged ions vastly reduces the probability of their direct chemical reaction. Therefore, still formally concordant with this type, reactions need a careful inspection of their mechanism. We feel that the study of primary salt effect on these reactions does not play the smallest role in this operation. It has to be mentioned that there are very few examples in the literature confirming the direct interionic reaction between the likely charged ions on the basis of the primary salt effect data. The

Table 1.

The Results of the Multilinear and Linear Least-Squares Treatment of the Primary Kinetic Salt Effect Data According to the Equations Following the Structural Theory of Electrolyte Solutions.

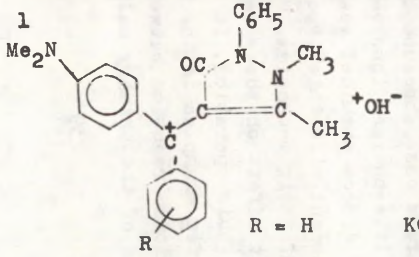
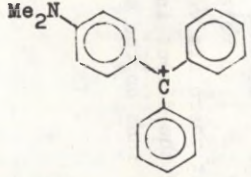
Reaction	Electrolyte added	No of equation	a'_t (theor)	$\ln k_o$ [b]	a_t [a]	Δ [b]	r [c]	s [d]	s_o [e]	Reference
2	3	4	5	6	7	8	9	10	11	12
1  R = H	KCl	15	-1.3443	0.728 ± 0.017	-1.373 ± 0.036	-	0.9990	0.013	0.026	20
R=4-N(CH_3)$_2$	KCl	15	-1.3443	-2.105 ± 0.024	-1.206 ± 0.051	-	0.9982	0.012	0.043	20
2.  + OH^-	KCl $NaNO_3$	15	-1.3443	3.216 ± 0.015	-1.537 ± 0.035	-	0.9977	0.024	0.022	21.

Table 1 continued

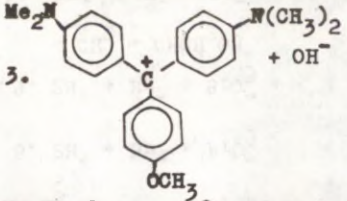
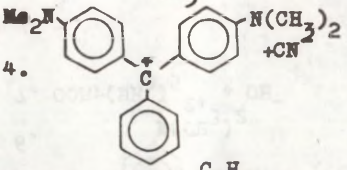
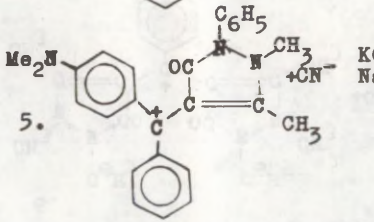
1	2	3	4	5	6	7	8	9	10	11	12
3.		KCl $NaNO_3$	15	-1.3542	0.567± 0.021	-1.375± 0.050	-	0.9967	0.027	0.036	18.
4.		KCl, $NaNO_3$	15	-0.5843	-0.315± 0.002	-0.629± 0.005	-	0.9997	0.002	0.008	19.
5.		KCl, $NaNO_3$	15	-0.5843	-0.339± 0.002	-0.588± 0.005	-	0.9998	0.001	0.008	19.

Table 1 continued

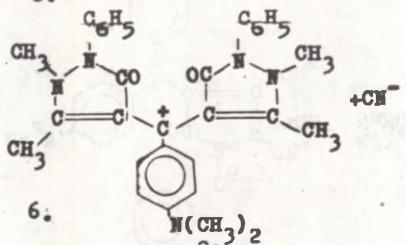
1	2	3	4	5	6	7	8	9	10	11	12
6.		KCl, $NaNO_3$	15	-0.5843[m]	-1.151±0.002[m]	-0.576±0.004	-	0.9998	0.001	0.008	19.
7.	$COBr(NH_3)_5^{2+} + OH^-$	NaCl	15	-2.6886	4.837±0.028	-2.543±0.014	-	0.9708	0.044	0.055	22.
		$BaCl_2$	15	-3.0780	4.828±0.033	-3.117±0.016	-	0.9825	0.028	0.041	22.
8.	$2H^+ + Br^- + BrO_3^-$	NaCl	13[a]	-2.6886	-0.619±0.020	-2.508±0.056	0.206±0.048	0.9996	0.018	0.010	23.
9.	$2H^+ + Br^- + BrO_3^- +$ $+ CH_2 = CHCH_2OH$	NaCl	13[a]	-2.6886	-0.488±0.029	-2.368±0.081	0.958±0.068	0.9983	0.026	0.020	24.
10.	$2H^+ + 2I^- + IO_3^-$	$NaNO_3$	13[a]	-2.6886	2.126±0.088	-2.690±0.066	2.514±4.766	0.9989	0.011	0.046	25.
		$NaNO_3$	15	-2.6886	2.081±0.018	-2.346±0.086	-	0.9986	0.009	0.036	25.

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12
		$KClO_4$	15	-2.6886	$2.076^{\pm}_{0.008}$	$-2.305^{\pm}_{0.040}$	-	0.9997	0.004	0.017	25.
		KNO_3	15	-2.6886	$2.114^{\pm}_{0.013}$	$-2.476^{\pm}_{0.063}$	-	0.9993	0.006	0.026	25.
		$LaCl_3$	15	-3.3874	$2.258^{\pm}_{0.040}$	$-3.355^{\pm}_{0.154}$	-	0.9979	0.020	0.046	25.
11.	$COBr(NH_3)_5^{2+}+Hg^{2+}$	HNO_3, KNO_3	17	5.3772	$3.851^{\pm}_{0.057}$	$5.584^{\pm}_{0.290}$	-	0.9766	0.086	0.051	22.
12.	$I^- + S_2O_8^{2-}$	KCl	17	1.1674	$-0.157^{\pm}_{0.008}$ *	$1.289^{\pm}_{0.042}$	-	0.9896	0.010	0.032	26.
		KCl, KI	17	2.6886	$-2.592^{\pm}_{0.016}$	$2.688^{\pm}_{0.076}$	-	0.9883	0.034	0.028	27.
13.	$BrCH_2COO^-+S_2O_3^{2-}$	KCl	17	2.6886	$-1.450^{\pm}_{0.016}$	$2.171^{\pm}_{0.083}$	-	0.9963	0.013	0.038	28.
		KCl, NaCl	17	1.1674	$-0.7822^{\pm}_{0.009}$	$1.107^{\pm}_{0.027}$	-	0.9953	0.017	0.024	29.
14.	$C_2H_5OOCNNO_2^-+ OH^-$	NaCl	17	1.3443	$-2.071^{\pm}_{0.033}$	$1.306^{\pm}_{0.084}$	-	0.9819	0.022	0.063	30.

(a This is the slope before the cube-root of electrolyte concentration and differs therefore by the z_+z_- from the a_t in formulae (13-15). a_t'(theor) is the theoretical slope.

(b Starred data correspond to the log k scale. Other results are given in lnk scale.

(c The correlation coefficient (b The standard deviation (c The normalized standard deviation(1

corresponding equation describing this effect is as follows:

$$\ln k = \ln k_0 - 2a_t z_+ z_- \sqrt[3]{c} + \Delta b \cdot c \qquad (16)$$

or in dilute solutions

$$\ln k = \ln k_0 - 2a_t z_+ z_- \sqrt[3]{c} \qquad (17)$$

where the notations are as used before (cf. Eq. (15)). The results of the data treatment according to Eqs. (16) and (17) for some reactions of the type discussed here are given in Table 1. (reactions 11-14). Again these are the typical reactions used for the confirmation of the Debye-Hückel approach to the primary salt effect. The results given in Table 1., however, assert that the fit with the predictions of the structural theory of electrolyte solutions is not by no means, worse.

The overall fit between the structural theory of solutions and experimental data is illustrated in Fig.4, which summarizes the results given in Table 1 by comparison of the theoretical concentration cube-root slopes with their experimental values. The value of the slope $tg\alpha = 1.028 \pm 0.036$ is equal to unity within the limits of errors (95% probability level). This graph is equivalent to the well-known LaMer picture[31] illustrating the validity of the electrostatic Debye-Hückel theory for the description of the primary salt effect and given in many monographs and textbooks. However, this presentation seems to be superior as it gives the results of the statistically obtained experimental slopes but not the visual picture for them.

Finally, we should like to recall a very important aspect of the interionic reactions. Namely, in the discussion made above it was assumed that the ionic reagents and activation complex are the uniform spherically distributed charges which can be approximated by the point charges. Still, for the many chemical reactions it is known in advance that the ionic charges in a particular reagent or activation complex are separated and fixed at a constant distance. Naturally, there is a substantial deviation from the spherical symmetry in the excess charge distribution along this multicharged ion and the simple model for the activity coefficient calcu-

latione presented by the structural theory of solutions[1,6] is not valid. However, it can be shown that analytical formulae for the activity coefficients of such ions are obtainable from the structural theory of solutions, and therefore for the primary salt effect with the participation of multicharged ions, too. These results of the data treatment of respective reactions will be published in our next communications.

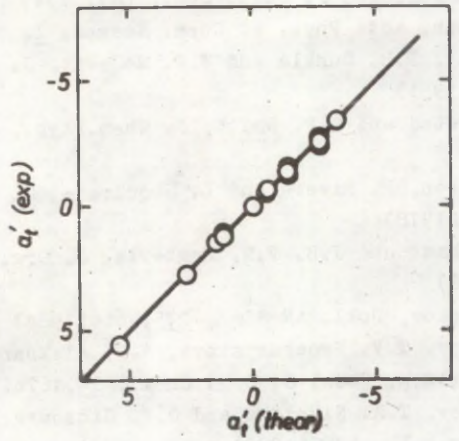


Fig. 4. The relationship between the experimental and theoretical slopes of the concentration cube-root dependence for the different interionic reactions.

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